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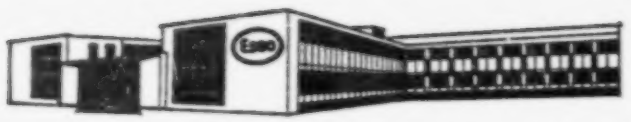

ESSO RESEARCH CENTRE

ABINGDON BERKSHIRE

INTERIM REPORT
(APCO CONTRACT CPA 70-46)

JUNE 22, 1970 TO FEBRUARY 22, 1971

STUDY OF CHEMICALLY ACTIVE FLUID BED GASIFIER FOR REDUCTION OF SULPHUR OXIDE EMISSIONS

J. W. T. Craig
G. L. Johnes
G. Moss
J. H. Taylor

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16. Abstracts

Batch reactor studies have extended the understanding of the Chemically Active Fluid Bed (CAFB) gasification process, the effects of its variables, and some of its limitations. A US fuel oil and one US limestone have been found to be satisfactory for the (CAFB) process, but a second US stone is not favorable. Two new batch reactors have been constructed, and an intensive variable study in them is underway. Construction is proceeding on a continuous CAFB gasification pilot plant scheduled for operation in mid 1971.

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TABLE OF CONTENTS

		Page No.
I.	SUMMARY	1
II.	BODY OF REPORT	3
	A. Introduction and Objectives	3
	1. Background Information	3
	2. Overall Project Objectives	5
	3. Current Work Objectives	5
	B. Apparatus and Procedures	6
	1. Batch Reactors	6
	2. Materials	15
	3. Batch Unit Experiments	16
	4. Continuous Gasifier Pilot Plant	17
	C. Results and Discussion	26
	1. Batch Reactor Studies	26
	2. Engineering Support Studies	49
	3. Programme for Batch Unit Variable Study	53
	D. Conclusions and Recommendations	56
	1. Conclusions	56
	2. Recommendations	57
III.	REFERENCES	58

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LIST OF FIGURES

Figure No.		Page No.
1	Modified Batch Gasifier	7
2	Photograph of 1-A Batch Unit	8
3	Batch Reactor Distributor Characteristics	9
4	Drawing of New Batch Reactors	13
5	Photograph of New Batch Units	14
6	Layout of Continuous Gasifier Unit	19
7	Material Balance and Flows, Continuous CAFB Pilot Plant	21
8	Test Rig for Bed Transfer Trials	22
9	Photograph of Cold Rig Model of Gasifier System	23
10	Successful Cyclone Fines Return Zone	24
11	Variation of Sulphur Recovery with Air/Fuel Ratio	28
12	Variation of Carbon Formation Rate with Air/Fuel Ratio	30
13	Variation of Sulphur Recovery with Carbon Formation Rate	30
14	Sulphur Recovery not Affected by Higher Air Velocity	32
15	Sulphur Removal Comparison for U.S. and U.K. Fuels	33
16	Sulphur Removal Curves at Different Air/Fuel Ratios	34
17	Regeneration of U.S. Limestone 1691	36
18	Bed Life Study (U.K. Fuel and Stone).	39
19	Cyclic Tests (U.S. Limestone 1691)	39
20	Cyclic Tests (U.S. Limestone 1690)	40
21 a	Photograph, Comparison of Distributors	41
21 b	Photograph, Agglomerates Recovered from Bed	41
22	History of Lime Losses in Cyclic Tests	42
23	Change in Particle Size During Cyclic Tests, U.K. Limestone	43

Continued...

LIST OF FIGURES(Continued)

Figure No.		Page No.
24	Change in Particle Size During Cyclic Tests, U.S. Limestone 1691	44
25	Change in Particle Size During Cyclic Tests, U.S. Limestone 1690	44
26	Vanadium Retention U.K. Fuel and Stone.	45
27	Vanadium Retention U.S. Limestone 1691	46
28	Vanadium Retention U.S. Limestone 1690	46
29	Concentrations of Sulphur in Regenerated Lime	48
30	Fluidsation Curves for Lime and Brick Dust	50
31	Results of Solids Transfer Tests	51
32	Air Consumption in Solids Transfer	52

I SUMMARY

Batch reactor studies have extended our understanding of the Chemically Active Fluid Bed (CAFB) gasification process, the effects of its variables, and some of its limitations. A US fuel oil and one US limestone have been found to be satisfactory for the CAFB process, but a second US stone is not favourable. Two new batch reactors have been constructed, and an intensive variable study in them is underway. Construction is proceeding on a continuous CAFB gasification pilot plant scheduled for operation in mid 1971.

A sample of Venezuelan fuel oil like that supplied to the northeastern United States was tested in the CAFB batch reactor with a fresh lime bed. It gasified well giving a highly combustible product that burned with a luminous flame. Sulphur removal efficiency began at 100% and fell with lime utilization at the same rate as observed with the UK test fuel under similar test conditions. This US fuel contains only 2.2% sulphur compared with 3.03% in the UK standard so that, on an absolute basis, it requires less limestone replacement than the UK fuel to maintain equal sulphur removal efficiency. The US fuel was judged to be satisfactory for CAFB operation, and a 2,000 imperial gallon supply was obtained for an intensive variable study.

Two US limestones were compared with a high purity UK stone in batch tests in which lime prepared from the stone was subjected to repeated cycles of gasification and regeneration. With a lime replacement rate of 0.75 wt. CaO/wt. S both the UK stone and the US stone BCR 1691 lined out at 72% sulphur removal efficiency, in good agreement with prior experience. Lime attrition and loss rate with stone 1691 was lower than with the UK stone. Stone 1691 contains only 81% of the CaO content of the UK stone but performs equally as well when replaced at an equal CaO/S ratio. The second US limestone, BCR 1690, is not satisfactory for CAFB gasification. It suffers high attrition rate, particularly in the initial cycle. It gives lower sulphur removal efficiency at equal CaO/S replacement rate (64% under conditions at which 1691 gave 72%) It has only 60% of the CaO content of 1691, and most serious, it sinters and agglomerates under CAFB conditions. A large supply of stone 1691 has been obtained for additional studies, but no further work is recommended on 1690 at this time.

Complete removal of vanadium from the fuel has been achieved with the UK stone and with both US stones. Although early indications had been that iron would have to be added to the lime to enhance vanadium recovery, such addition was not required.

Early indications that operation with 4 ft/sec superficial air velocity and no fuel combustion beneath the air distributor would permit 100% sulphur removal at air/fuel ratios as low as 20% of stoichiometric have not been confirmed. The established trend is for sulphur removal efficiency to fall as air/fuel ratio is reduced below about 25% of stoichiometric. Although occasional high efficiencies have been obtained at lower air fuel ratios, the conditions for reproducible high efficiency at 20% of stoichiometric air have not been established. At 10% of lime reacted and 20% of stoichiometric air, the average sulphur removal

efficiency is near 80%. Indications are that the cause of reduced sulphur removal at low air/fuel ratio is the rapid increase of carbon content of the bed.

Most of the oxygen supplied to the gasification process is consumed by combustion of carbon. With about 24% of stoichiometric air, about 40% of the carbon from the fuel is oxidised compared with only about 10% of the hydrogen.

Most of the work to date has been conducted with an air superficial velocity of 4 ft/sec. However, a test at 4.8 ft/sec showed no deterioration of sulphur removal efficiency. Higher gas rates will be tested in the newly constructed batch units.

Solids transfer testing in a cold model of the continuous gasifier pilot plant has provided information for design of a simple but effective solids circulation system. This design has been incorporated in the continuous unit which is being constructed. Assembly and refractory pouring for the continuous unit has been completed with firing of the refractory scheduled for the final week of February.

Combustion of the hot CAFB gasifier product requires a different burner design from the usual gas burner because of the much higher gas/air volumetric ratio. Several designs have been tested on batch gasifier units to provide data for design of the continuous unit burner.

The immediate work programme in the new batch units consists of a series of fresh bed tests to define effects of air/fuel ratio, temperature, gas velocity, lime particle size and bed depth with the US fuel oil and limestone 1691.

The fresh bed tests will then be followed by cyclic gasification regeneration studies to define effects of lime replacement rate at selected sets of conditions.

II BODY OF REPORT

A. Introduction and Objectives

Exploratory work at the Esso Research Centre, between 1966 and 1970, had shown a range of conditions under which sulphur is trapped by a shallow fluidised bed of lime in which fuel oil is undergoing partial combustion and gasification. The possibility of regenerating the lime had also been demonstrated. Thus the framework had been established for a process to eliminate SO_2 pollution during combustion of high sulphur fuel oils. The process is designated CAFB for Chemically Active Fluid Bed.

The process employs a shallow (1 to 2 ft. deep) fluidised bed of lime in a gasifier to partially oxidise, gasify and completely desulphurise the heavy fuel oil. The gasified, sulphur-free, fuel passes from the fluid bed to the burners of a boiler. The calcium sulphide which forms in the gasifier is converted back to calcium oxide in a fluid bed regenerator by contact with air. A small purge stream of lime is replaced by fresh limestone to maintain activity of the lime bed.

The sulphur leaves the system as 10-15% sulphur dioxide in the hot gas from the regenerator. This SO_2 can be recovered in several ways; for example, by conversion to sulphuric acid or by direct reduction to elemental sulphur.

In addition to eliminating SO_2 pollution, the process has the additional benefit of removing vanadium before the boiler and eliminating this source of high temperature corrosion.

In June 1970, Esso Research Centre began work on a contract with the National Air Pollution Control Administration to study the CAFB gasifier process for possible application in the United States. This is an interim report on the work done under this contract in the period from June 22nd 1970 through February 22nd 1971.

1. Background Information

The first tests at Esso Research Centre on fluid bed combustion of fuel oil were performed with the goal of achieving improved heat transfer rates in oil utilisation. It soon became evident that by using lime as the fluid bed medium, benefits in pollution abatement could be obtained which potentially were more important than the improved heat transfer. It was found that sulphur was trapped by lime both under fully combusting conditions and under gasifying conditions. In the latter case the oil is contacted with substoichiometric amounts of air, and the gasifier product is a hot, sulphur-free fuel gas which can be burned in a conventional boiler.

Under fully combusting conditions the sulphur reacts with lime to form calcium sulphate.

$$H_2S + 2O_2 + CaO \longrightarrow CaSO_4 + H_2O$$

The sulphate can be reduced to SO_2 and lime with fuel oil. The reduction with hydrogen is:

$$CaSO_4 + H_2 \longrightarrow CaO + SO_2 + H_2O$$

When fuel is combusted under substoichiometric conditions, the sulphur is trapped by lime as calcium sulphide:

$$H_2S + CaO \longrightarrow CaS + H_2O$$

The lime can be regenerated by oxidising the CaS with air:

$$CaS + 3/2\,O_2 \longrightarrow CaO + SO_2$$

Each pair of reactions forms the basis of a regenerative lime process for avoiding SO_2 pollution when using high sulphur fuel oil. The gasifier process has the added advantage that it is potentially applicable to existing power plant installations.

The early work was described in a technical proposal to NAPCA[2] in 1969. Later work obtained in the period between submission of the proposal and beginning of work under NAPCA contract CPA-70-46 is summarised in Appendix A of this report.

Although the CAFB process uses continuous circulation of solids between two fluid bed reactors, the experimental work used a single reactor in which conditions were cycled between gasification and regeneration conditions. The earlier tests used reactors without cyclones and were restricted to low gas velocities to prevent solids carryover. Later versions of the apparatus employed internal cyclones and were able to use higher gas velocities. Temperatures in the range of 800-900°C were found best for sulphur removal during gasification. The regeneration of sulphided lime occurred between 1,000 and 1,100°C.

With the low gas velocity reactor it was necessary to underfire - that is, to burn some fuel in the plenum space beneath the air distributor. If underfiring were not used, the velocity of the cold entering air was insufficient to fluidise the solids in the vicinity of the distributor, and poor desulphurising efficiency was obtained. Even with underfiring, desulphurising efficiency declined severely as air to fuel ratio decreased below 30% of stoichiometric. When reactors with cyclones were employed, higher total gas rates could be employed, and underfiring was no longer required. Under these conditions, good sulphur removal was obtained at air rates down to nearly 20% of stoichiometric.

When a single bed of lime is cycled between gasification and regeneration conditions there is a gradual loss of sulphur removal efficiency. If a portion of the lime is replaced with fresh limestone at the beginning of each cycle, the efficiency will line out at some level which depends on the quantity of lime replaced. A curve of lined out efficiency vs. lime replacement rate was established which indicated that replacement of about 1.75 wt. of CaO per wt. of sulphur

fed would maintain the sulphur removal efficiency at close to 100%. These bed life tests had been made with underfiring and about 30-35% of stoichiometric air.

During these bed life tests, the retention of sodium and vanadium from the bed was measured. Sodium pick-up was less than 20% of the amount introduced. Vanadium pick-up was variable, and appeared to change with the amount of iron picked up from steel components of the equipment. As discussed later, this dependence of vanadium pick-up on iron was not been borne out in our recent work. In fact, the recent work shows complete vanadium retention in all instances.

2. Overall Project Objectives

Work under this contract constitutes Phase I of an overall project, the objective of which is the demonstration and evaluation of the CAFB process in a converted power generation boiler of 100-150 megawatt capacity. The objectives of this Phase I study are:-

(a) Survey operating characteristics of two limestones and one residual fuel oil selected by NAPCA for use in a CAFB process.

(b) Select one limestone for further testing with the fuel oil

(c) Assess the effects of important operating variables on sulphur sorption-regeneration using the US fuel and the selected limestone

(d) Operate for 200 hours, at conditions based on the batch unit variable study, a continuous pilot scale CAFB gasifier designed and constructed at Esso's expense.

3. Current Work Objectives

Specific objectives of work covered by this interim report have been as follows:-

(a) Determine the performance of the US fuel oil in CAFB gasification.

(b) Compare operating characteristics of two US limestones supplied by NAPCA and select one for further study.

(c) Construct two new CAFB batch units for use in the intensive variable study with the selected fuel-limestone combination.

(d) Provide guidance to assure performance of the continuous gasifier designed and constructed by Esso.

(e) Screen the effects of operating variables to select the range of conditions to be used in the intensive variable study.

B. Apparatus and Procedures

Apparatus and procedures used in this study are described in this section. The apparatus includes the batch unit used in most of the experimental work to date, two new batch units which have recently been completed, a cold, full size, model of the continuous gasifier, and the continuous gasifier pilot plant which is now under construction. Materials employed include two fuel oils, three limestones and a brick dust used to simulate hot lime in the cold gasifier model.

1. Batch Reactors

A batch reactor built by Esso was in existance when the research contract was signed with NAPCA. This unit has been used for most of the experimental work on the CAFB reaction performed in this report period. During this period, two new batch units have been designed and constructed.

(a) The 1-A Batch Reactor

The batch reactor used in the CAFB tests during most of this period is designated No. 1-A. The lower section of this unit was the first CAFB reactor used extensively at the Esso Research Centre. In those original tests, however, it was not fitted with cyclones, and therefore was used only in low gas velocity experiments. Before the current work began the unit was fitted with an expanded upper section and an internal cyclone. This cyclone, which is closed at the bottom, traps fines but does not return them to the fluid bed. The quantity of fines is withdrawn and measured at the end of each run period. A drawing of the 1-A reactor is shown in Figure 1, and a photograph in Figure 2.

The reactor is made of a carbon steel shell lined with a high temperature castable refractory. The lower section, which contains the fluid bed, is 7-inches internal diameter, by 33 inches high. The upper section expands to 15 inches internal diameter and serves as a disengaging space for all but the finest particle size range of solids.

The distributor is a "top hat" design with a raised section 5 inches in diameter. It contains sixteen horizontal holes distributed around its circumference.

MODIFIED BATCH GASIFIER

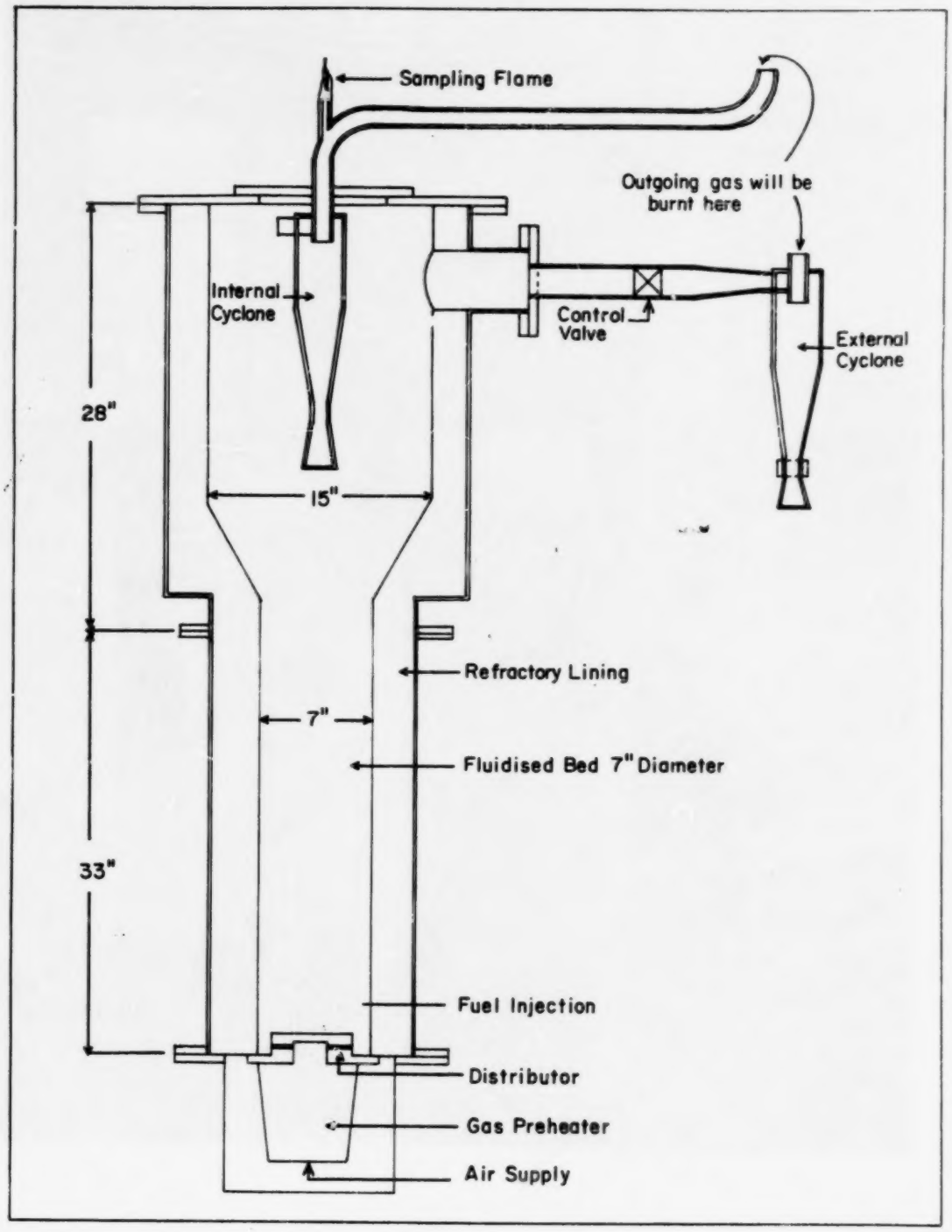


FIGURE 1

PHOTOGRAPH OF 1-A BATCH UNIT

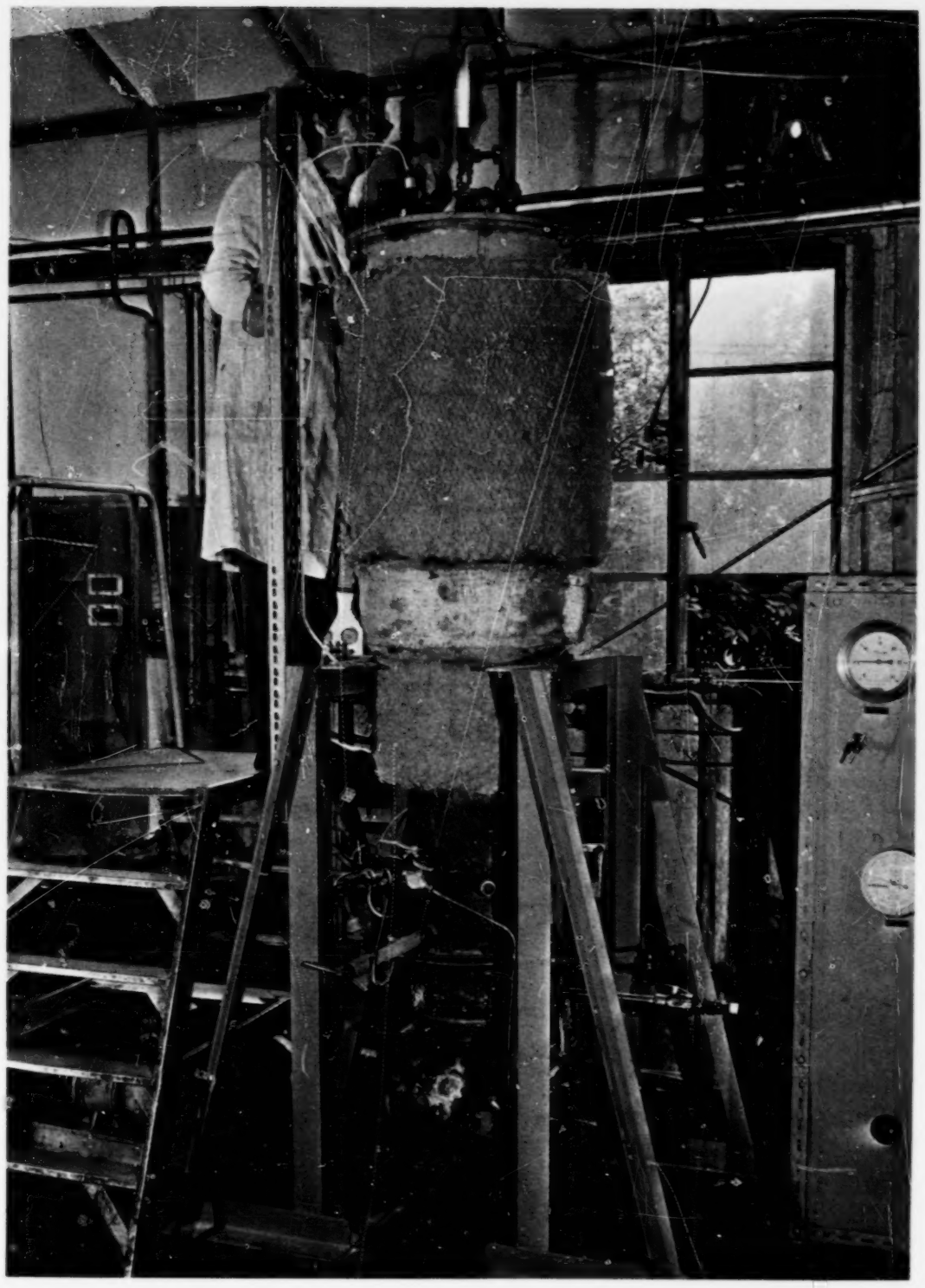


FIGURE 2

A low pressure drop distributor with 3/16 inch diameter holes has been used for most of the work, but a higher pressure drop distributor with 1/8 inch holes has also been tested. Pressure drop characteristics of the two distributors are shown in Figure 3.

BATCH REACTOR
DISTRIBUTOR CHARACTERISTICS

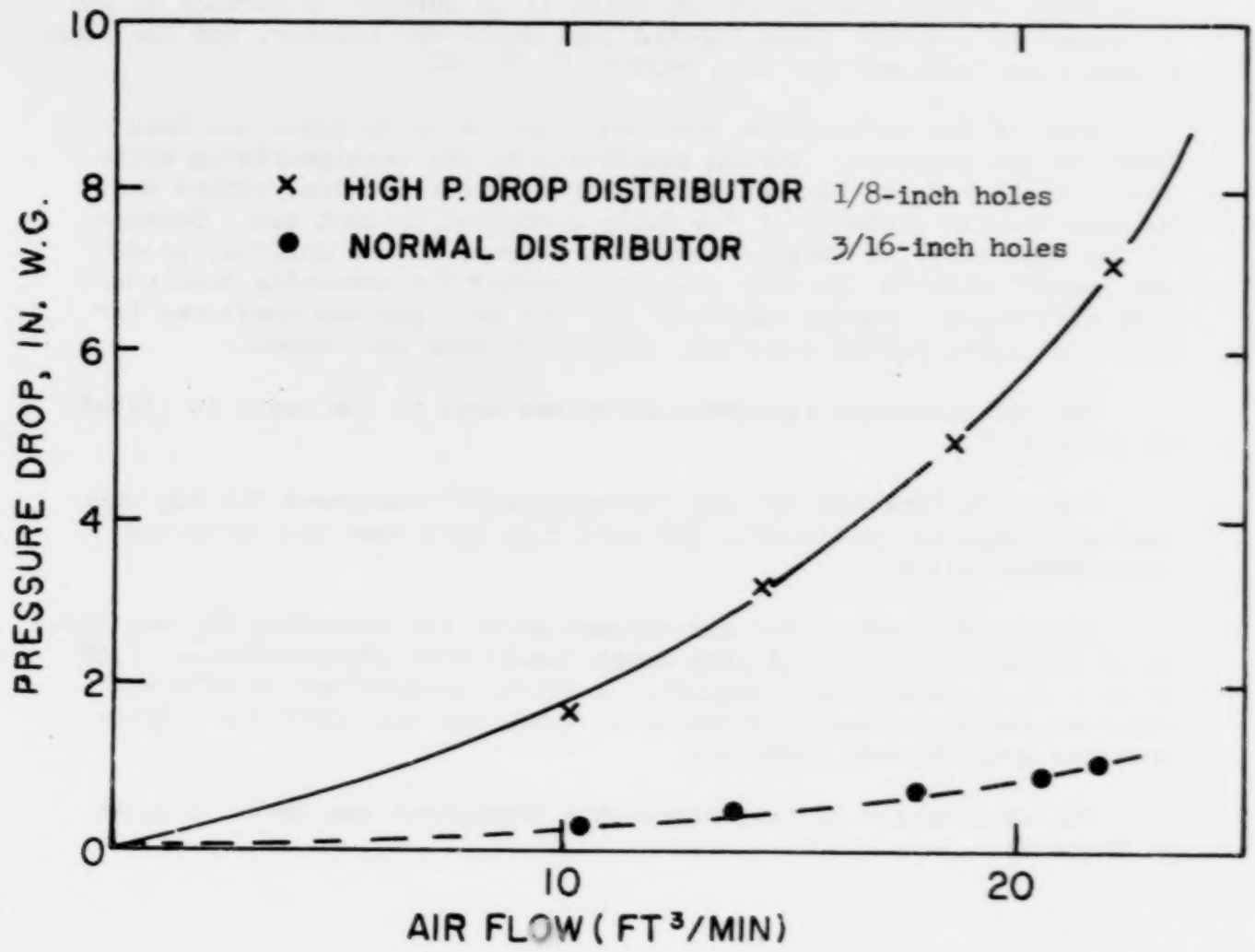


FIGURE 3

Fuel oil enters the reactor through a single 1/4 inch nozzle which normally protrudes one inch in from the reactor wall, and 5 1/2 inches above the bottom. In some tests the fuel injector was extended to the reactor centre, but results were unsatisfactory as the fuel entered a poorly fluidized region. A small flow of air, normally one cubic foot per minute, enters with the fuel to decrease oil residence time in the nozzle and to aid in oil dispersion.

The 1-A unit has no provision for temperature control other than by adjusting the quantity of insulation around the reactor. This insulation was arranged to permit the unit to operate in the range of 800 to 900°C with air velocity of 4 ft./sec. and air/fuel ratios in the range of 20 to 30% of stoichiometric. With constant air supply, the unit tends towards 900° at the lower fuel rate and 800° at the higher rate.

(b) Gas Analysis

Product gas leaves the unit through the cyclone outlet and passes to a flare outside the laboratory where it is burned. A portion of gas is burned in a sample flame located just above the reactor, and the combustion products are analysed for SO_2, oxygen, CO and CO_2.

Most of the information obtained from the batch tests has been based on gas analysis. During gasification, the desulphurising efficiency of the bed has been calculated from carbon dioxide, oxygen and sulphur dioxide contents of the fully combusted product gas. Because of the wide range of sulphur compounds present in the gasifier product gas itself, this is the only practical method for measuring desulphurising efficiency. During regeneration, the exit gas was monitored for carbon dioxide, carbon monoxide, sulphur dioxide and oxygen.

The gas analysing equipment which was used in the tests is listed in Table I.

The conductimetric and gas chromatographic analysers for SO_2 were basically back-up instruments and were only used when the infra-red instruments failed.

The column used in the gas chromatograph for measuring SO_2 was made up of diethylene glycol adipate cross linked with pentaerythritol (10% by wt.) on a chromosorb P support. A column temperature of 80°C was employed for SO_2 concentrations up to 3,000 ppm and 100°C for concentrations greater than 3,000 ppm.

The utilisation of the instruments throughout the tests is shown in Table II.

TABLE I

GAS ANALYSING EQUIPMENT

Analyser	Type	Manufacturer	Model	Response	Range
SO_2	Infra-red	Maihak	Unor 6	Continuous	0-3,000 ppm
SO_2	Infra-red	Maihak	Unor 6	"	0-20 % by vol.
SO_2	Conductimetric	Wostoff	-	"	0-500 ppm
SO_2	Gas Chromatographic	Pye	Series 104	Intermittent	0-100% by vol.*
CO_2	Infra-red	Maihak	Unor 6	Continuous	0-20 % by vol.
CO	Infra-red	Maihak	Unor 6	"	0-20 % by vol.
O_2	Paramagnetic	Servomex	OA 137	"	0-25 % by vol.

* Variable range

TABLE II

INSTRUMENT UTILISATION

Runs	SO_2 (IR Low Range)	SO_2 (IR High Range)	CO_2 (IR)	CO (IR)	O_2 (Paramagnetic)	SO_2 (Conductimetric)	SO_2 (GC Low Range)	SO_2 (GC High Range)
1 -32	✓	✓	✓	✓	✓	-	-	-
33-40	✓	✓	✓	-	✓	-	-	-
41-43	-	-	✓	-	✓	-	-	-
44-53	-	-	✓	-	✓	-	✓	-
51-72	-	-	✓	-	✓	✓	✓	-
73-108	-	-	✓	-	✓	✓	-	✓
109 -121	-	-	✓	-	✓	-	✓	-

(c) Batch Unit Operating Procedures

The operating procedures followed in the tests are described below:-

(1) Start-up

The bed was heated to operating temperature by combusting butane below the distributor. The procedure followed was, first of all, to raise the temperature of the bed space to 950°C, and then, after shutting off the butane and fluidising air, to add approximately 9 lbs of bed material. The temperature was again raised to 950°C and these steps repeated until all the bed was at a temperature of 950°C.

(2) Calcination

The start up procedure was also followed for calcination. Due to the strongly endothermic nature of the reaction, 950°C could only be attained when all the carbon dioxide was driven off. CO_2 emissions were also checked by gas analysis.

(3) Gasification

When the start-up procedure had been completed, the fluidising air was set to the desired level. The butane supply was terminated and the fuel oil flow, which had been set during start-up, was immediately switched on. The sampling flame burner and external flare were lit and the gas analysers connected. Relevant data was recorded and bed samples taken from a point 7" above the distributor at prescribed intervals. Bed sampling was carried out under nitrogen to prevent any oxidation of the sulphided lime.

(4) Regeneration

For regeneration, the fuel supply was switched off and air, alone, allowed to contact the bed. The gas analysers were switched to the sampling system for regeneration and the relevant data collected. A bed sample was collected after each regeneration.

(5) Shut-down

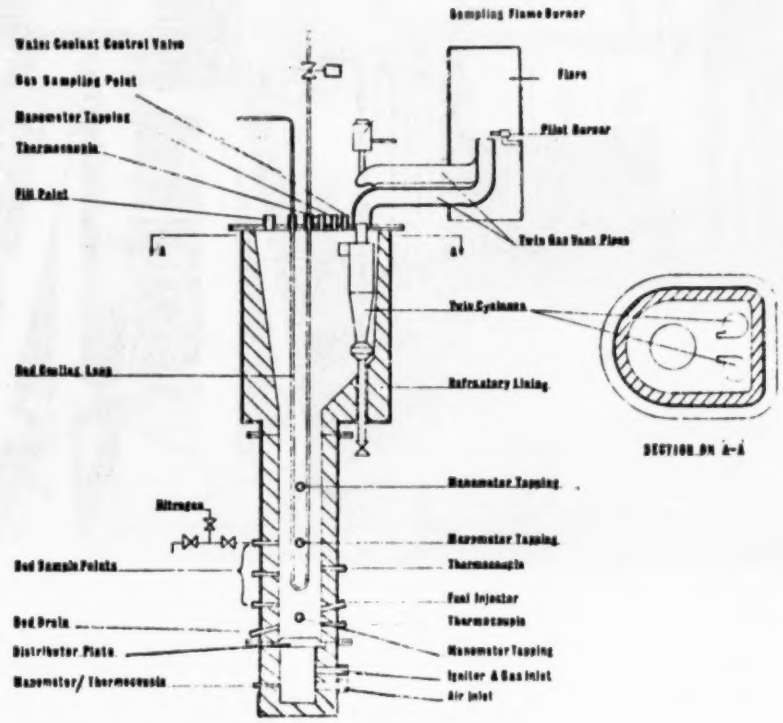
The bed temperature was allowed to drop to 700°C before the bed was removed through the drain point just above the distributor. Draining the unit is much easier when the bed is hot since the solids flow better under these conditions. When all the bed had been removed, the cyclone was emptied and all ancillary equipment shut-off.

(d) Two New Batch Units Constructed

In order to increase the rate at which batch variable studies can be conducted, two new units have been designed and constructed. The lower sections of these units are identical to that of the 1-A unit. The upper sections were redesigned to permit installation of two internal cyclones and to allow drainage of the cyclones to external sample collectors during operation.

The new reactors contain internal cooling coils which will permit control of reactor temperature independently of fuel and air rates.

Figure 4 is a drawing of the new reactor with its various inlets and connections. Figure 5 is a photograph of the two batch units with their control panel. These units have been designated No. 4-A (left hand unit facing panel) and No. 4-B.



C.A.F.B. BATCH UNIT
REACTOR

FIGURE 4

PHOTOGRAPH OF NEW BATCH UNITS

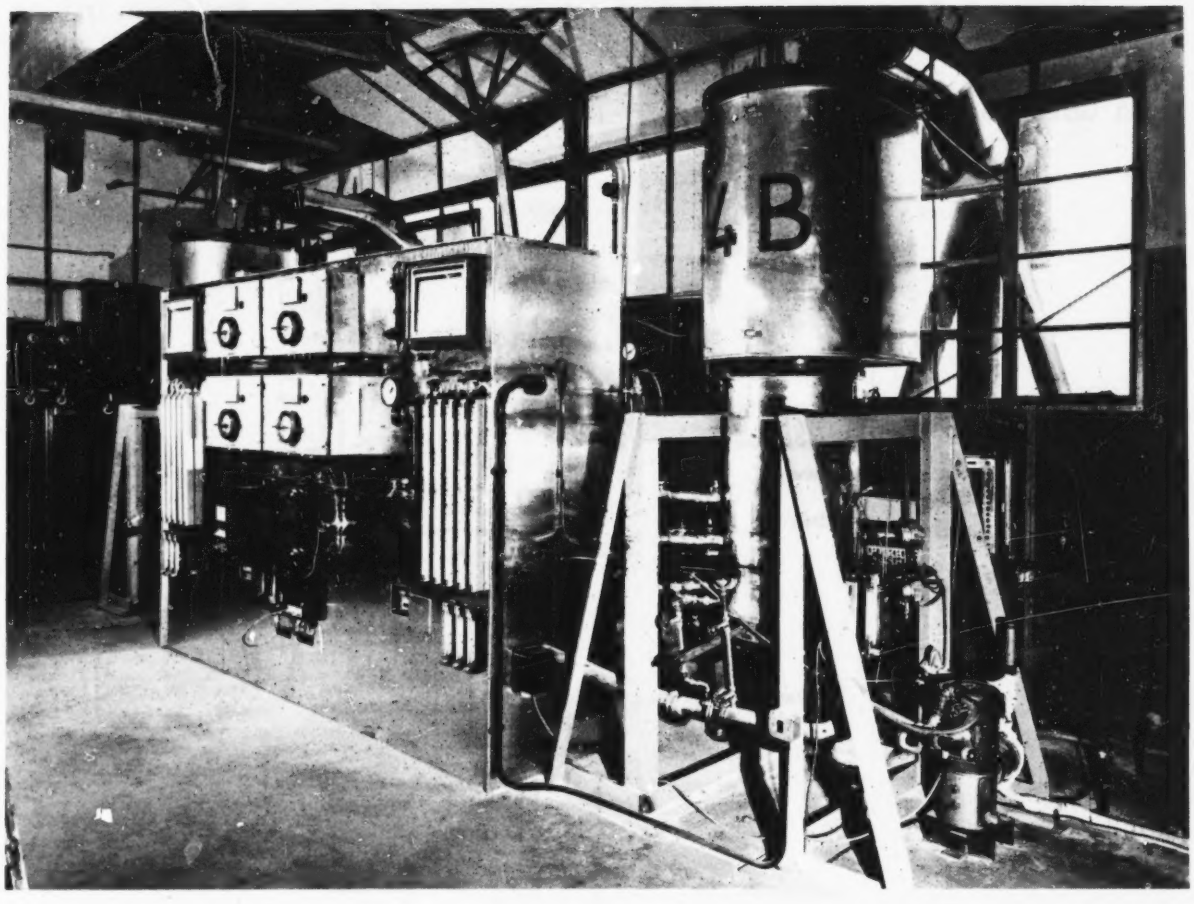


FIGURE 5

Assembly of the units was completed in January and calibration started. Operation of these units with US fuel oil and limestone began in mid-February.

2. Materials

A high purity Denbighshire limestone had been used as the standard CAFB reagent for studies prior to beginning work under the NAPCA contract. Much of this work was also performed with a fuel oil blend available in large quantities at the Esso Research Centre. These materials have also been used in the current work to provide a basis of comparison with the US fuel oil and limestones now under study. Properties of these limestones and fuels are tabulated in Appendix B. They are summarised below in Tables III and IV.

TABLE III

LIMESTONE ANALYSIS

Limestone:	UK Denbighshire	US 1691	US 1690
Component:			
CaO	55.2	45.0	26.7
MgO	0.27	2.02	17.5
SiO_2	0.32	14.2	13.5
CO_2 released	43.4	35.4	35.5

TABLE IV

FUEL OIL ANALYSIS

Property	UK Test Fuel	US Test Fuel
Specific gravity	0.95	0.95
Sulphur, % by wt.	3.03	2.22
Vanadium, ppm	140	270
Conradson Carbon, % by wt	9.32	7.5

(a) Limestone

The UK limestone used in past studies is a relatively high purity material quarried in Denbighshire in Northern Wales. When calcined it gives a lime containing 97.5% CaO. The two US limestones supplied by NAPCA were shipped in steel drums and crushed and screened at Esso Research Centre. Both US stones were of lower calcium oxide content than the Denbighshire stone and represent classes of stones available in larger quantities than the high purity stone. The stone designated 1690 in the Bituminous Coal Research Inc. (BCR) listing comes from Ogdensburg, New York. It has the lowest calcium content of the three stones tested and is high in both magnesia and silica. The stone BCR 1691 comes from Seneca Falls, New York, and also has high silica but little magnesia. It is intermediate in calcium content and is similar in composition to Pennsylvania "cement rock".

(b) Fuel Oil

The UK fuel oil which has been used as a standard for a great deal of the CAFB work is a blend of Middle Eastern and Venezuelan oils which has relatively high levels of both vanadium and sulphur. The US fuel oil is Venezuelan, from Amuay Refinery of Creole Petroleum Co. It has the high vanadium content typical of Venezuelan oil, but is lower in sulphur content than the UK blend. The analysis shown in Table IV is based on the one drum sample supplied in June 1970. Subsequently an additional 50 drum supply has been obtained.

3. Batch Unit Experiments

Two principal types of experiments are performed in the batch units; fresh bed tests and multi-cycle tests. The purpose of fresh bed tests is to determine the effect of process variables on the initial sulphur removal efficiency and on its maintenance for a prolonged period with a single lime charge. The cyclic tests which consist of many cycles of gasification and regeneration with partial lime replacement between cycles are intended to measure the extent of lime deactivation which will take place during continuous operation.

In our data system each cycle has been given a separate run number. A total of 121 run cycles has been completed in this report period. Run conditions and results are tabulated in Appendix C. Results are discussed in Section II-C.

The first twenty five tests were commissioning runs on the newly modified 1-A unit to compare its performance with earlier results. Included in this series was a test with the US fuel and UK lime (Run 23) to determine if the US fuel would present any operating difficulties. It did not. These early tests indicated that the fuel injector nozzle was improperly positioned. It was repositioned and the series of fresh bed tests continued. Runs 26 through 32 were made at low stoichiometric air rates to determine the effects of oil injection variables on carbon formation in the bed and to determine the minimum practical air/fuel ratio for a cyclic test to demonstrate bed life.

Tests 33 through 53 were 21 cycles made with UK limestone and fuel at 4 ft./sec. superficial air velocity, 24% of stoichiometric air rate and 0.75 wt. CaO/wt. S replacement rate to determine if the 1-A unit gave the same lined out desulphurising efficiency as had been obtained in the earlier units with bed underfiring, and to provide a base line for comparison with US limestones. No underfiring was used in this test series.

Tests 54 through 72 were 19 cycles made with US limestone 1691. Conditions were the same as used in the cyclic test with Denbighshire stone. Tests 73 through 77 were made with US limestone 1690 in an attempt to test it under conditions comparable with those used for the Denbighshire stone and US stone 1691. High attrition losses in the early cycles made this impossible, and the cyclic tests were restarted at a higher lime make-up rate. This series consisted of runs 78 through 95.

Runs 96 through 109 were fresh bed tests with the higher pressure drop distributor to see if this distributor would improve desulphurisation as air/fuel ratio was reduced to near 20% of stoichiometric. This series included a test athigher (4.8 ft./sec.) air velocity and a test with US fuel and US limestone 1691. Unfortunately cracks developed in the reactor lining during this series and obscured the results.

The effects of distributor pressure drop were investigated with a relined reactor in tests 110 through 121 which also were fresh bed tests.

4. Continuous Gasifier Pilot Plant

A continuous CAFB gasifier pilot plant is under construction at the Esso Research Centre to provide a demonstration of the CAFB process under continuous operating conditions and to provide a means of studying those operational variables which cannot be measured in batch reactors. As part of the contract with APCO this pilot plant will be operated for 200 hours under conditions selected as near optimum from the batch reactor variable study.

(a) Design basis for the Size and Layout of the Experimental Gasifier

The size of the experimental gasifier was determined by the decision to adopt dimensions for the regenerator virtually identical with those of the batch unit. This decision was taken on the grounds that this was a proven design which had operated under regeneration conditions in a satisfactory manner at the gas velocities which were envisaged.

Since experience had also shown that the SO_2 concentration in the regenerator tail gas would be in the region of 10% by volume, the sulphur throughput of the unit, under conditions which had actually been used, was limited to 8.6 lbs/hr. In the case of a 2.2% by wt. sulphur fuel the fuel throughput was therefore restricted to 391 lbs/hr. giving an output of 7.1 MM Btu. gross or 6.68 MM Btu. net, per hour. At 20% of stoichiometric air and a gas velocity of 4 ft/sec. at 900°C this indicated a cross-sectional area for the gasifier of 4.8 sq. ft.

At an early stage in the design of the installation it was decided to use the gasifier to fire a conventional packaged hot water boiler. It was considered advantageous to show that the gasifier could be used in conjunction with commercially available equipment and the installation lent itself readily to the employment of flue gas recycle as a means for controlling the temperature of the gasifier bed. The boiler also provided a suitable test chamber for the development of the gas burner. This was a necessary requirement since no burner handling this type of gas is in current commercial use.

The actual geometric configuration of the gasifier was very largely influenced by the decision to build it as a monolithic structure in refractory concrete. A major advantage of this method of construction is that it allows heat to be conserved in the transfer system between the two fluidised beds. It also allows the beds to be positioned very

close to each other, so reducing the overall size of the unit. Disadvantages arise from the fact that the unit is very difficult to modify once the concrete has been poured. In addition considerable reliance is placed on the durability of the concrete, since the development of cracks in the walls between the gasifying and regenerating beds could adversely affect performance.

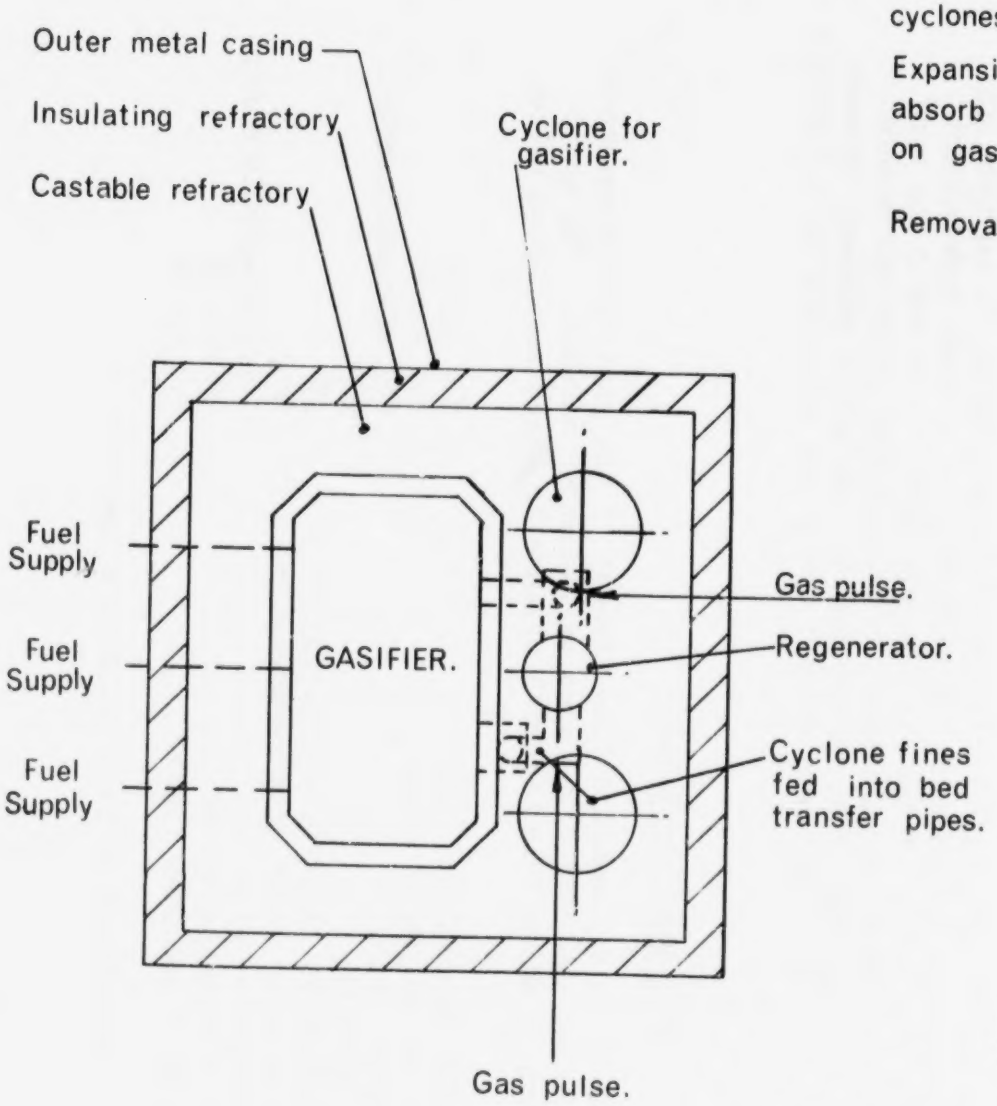
This precise form of construction is not recommended for general use but was considered appropriate to the case of a small experimental unit of limited life. Every effort was made to obtain the best advice available in choosing the refractory material and in developing a detailed design for the refractory block.

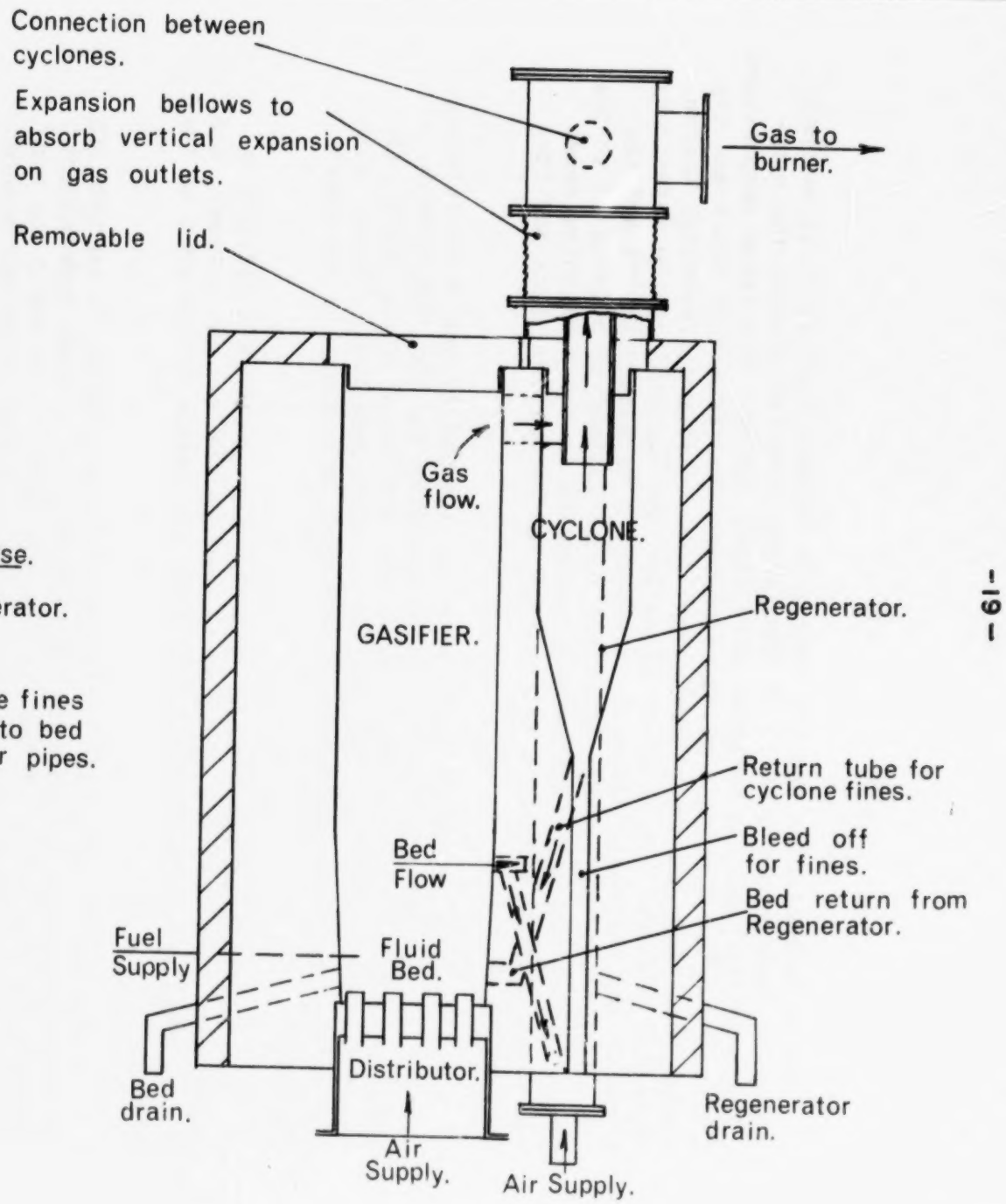
The geometrical configuration of the gasifier was determined largely by the need to accommodate cyclones for the desulphurised gas stream. It was found that the choice of a single cyclone resulted in an awkward layout and increased the overall height, and therefore cost, of the unit. For this reason two cyclones were used in parallel to give the layout shown in Figure 6. Since the cyclones consisted merely of holes cast in the refractory block it cost very little more to provide two small cyclones in place of one large one, and the extra expenditure on cores was more than offset by the saving due to the reduction in the overall size of the gasifier.

The cyclones were positioned one on each side of the regenerator. This allowed the use of a rectangular gasifier bed and resulted in a compact design. Another advantage of this layout was that it resulted in a simple ducting system for the transfer of bed material. Once the cyclones had been positioned either side of the regenerator it seemd reasonable to make use of the bed transfer system in order to drain them of fines. In the arrangement which was adopted half of the fines from the gasifier are returned to the gasifier bed, the remainder being fed to the regenerator. The regenerator cyclone, which is an external fitting, is used to drain fines from the unit.

Another question which had to be considered was the manner in which the gasifier should be brought to its working temperature. The small batch units are initially fired with LPG beneath their distributors. This procedure results in an excessive pressure drop across the distributor under starting conditions, and also imposes thermal stresses on its structure. For these reasons it was decided to position the starting burner above the distributor of the gasifier in such a way that it acted as a submerged combustor in the fluidised bed. Since with this arrangement the underside of the distributor was always cold the distributor could be constructed of steel.

In order to facilitate any necessary repairs or alterations to the distributor it was designed for easy removal , and adequate ground clearance was allowed beneath the gasifier for this purpose.





LAYOUT OF CONTINUOUS GASIFIER UNIT.
FIG. 6.

Since refractories are not very good thermal insulators it was necessary to incorporate a shell of insulating material between the monolithic gasifier and its external mild steel casing. The large temperature difference under working conditions between the refractory block and its casing resulting from this arrangement introduced a differential thermal expansion problem. In order to allow for the "growth" of the refractory block in the vertical direction it was found necessary to "float" the lid of the gasifier on the refractory block instead of bolting it to the flange of the casing. Differential expansion in the horizontal sense was dealt with by leaving a gap between the refractory block and its insulating shield.

The need to accommodate differential thermal expansion dictated the designs of the offtakes from both the gasifier and the regenerator. The simplest possibility which presented itself was to run these offtakes through the lid of the gasifier so that they could "float" with the refractory block and not be constrained in any way by the steel casing.

In the case of the outlets from the main cyclones a refractory lined arch-like duct was designed to combine the two gas streams, and a single pipe was run horizontally from the centre of the arch to the burner.

Since the floating lid of the gasifier was unable to sustain any externally applied stresses it was necessary to provide independent support for the weight of the ducting and burner. It was found convenient to provide a portal frame for this purpose which was mounted on the projecting base frame of the boiler. Relative movement between the burner and the boiler was catered for by the provision of a flexible sealing bellows.

(b) Basis and Flow Rates

Figure 7 is a schematic flow diagram of the gasifier-regenerator system showing the mass flow rates of the major streams. The basic assumptions on which this material balance is based are listed below.

Sulphur throughput	8.6 lb/hr
Fuel oil sulphur content	2.2 wt. %
Air/fuel ratio	20% of stoichiometric
US limestone	1691
% sulphur in lime* from gasifier	5%
% sulphur in lime* from regenerator	1%
Lime make-up rate	1 mole CaO/mole S fed
SO_2 in regenerator off gas	10 mol. %
Carbon on gasifier lime*	0.3 wt. %

* Lime taken as Ca + O + S in stone

MATERIAL BALANCE AND FLOWS
CONTINUOUS CAFB PILOT PLANT
(ALL FLOWS IN POUNDS/HR)

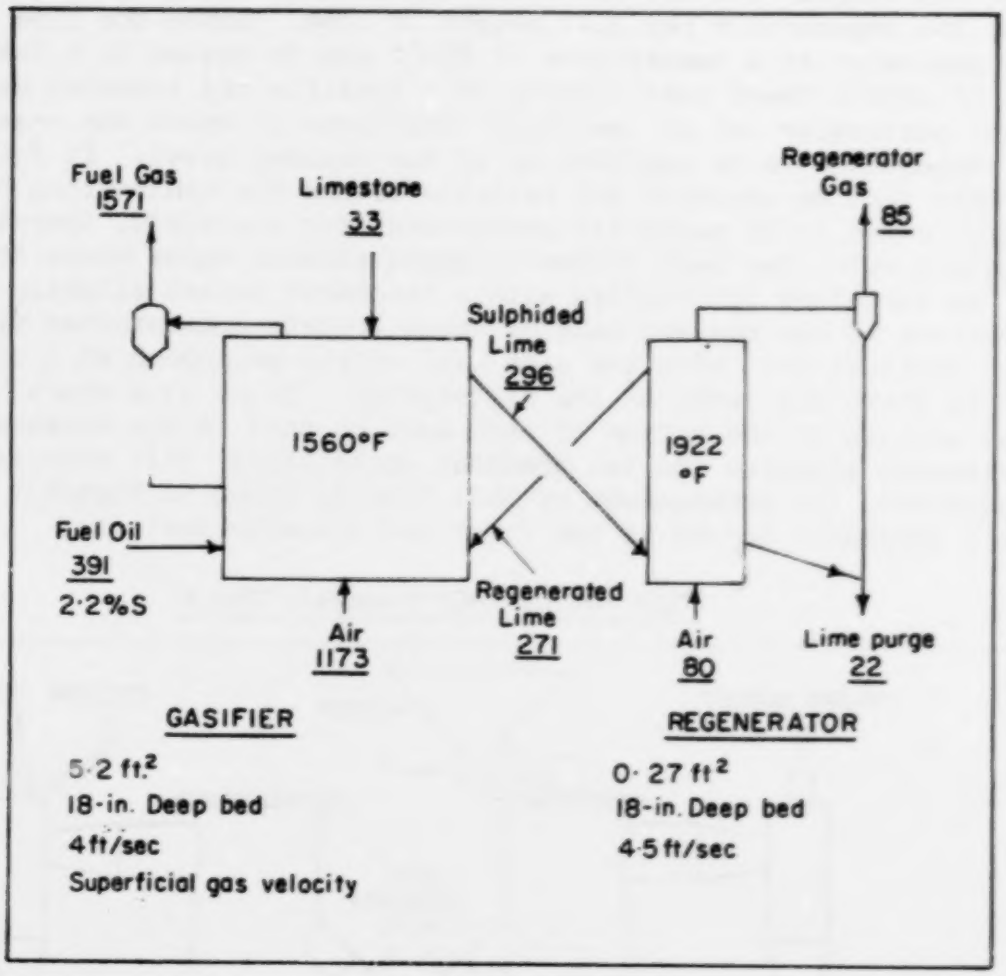


FIG. 7.

(c) Principles of Gasifier Control

If the gasifier is to function efficiently it is necessary to maintain the temperature of the gasifying bed in the region of 850°C whilst the temperature of the regenerating bed must lie in the region of 1050°C. Should the temperature of the regenerating bed fall below 800°C recarbonation will occur, and the effect of this will to lower the temperature of the regenerator. If the gasifying temperature rises above 900°C then the desulphurising efficiency will be reduced. In the case of the regenerator too low a temperature will result in the formation of calcium sulphate and a build-up of sulphur in the bed material, whilst too high a temperature may tend to deactivate the lime. A method of controlling the temperatures of the two beds has been chosen which involves no heat losses and no heat transfer surfaces. In the case of the gasifying bed it is proposed to control the temperature by recycling some of the flue gas formed by complete combustion back to the inlet of the air blower. This necessitates a separate air supply for the regenerator. In the case of the regenerator the temperature will be controlled by varying the circulation rate of the bed material. The rate of heat release in the regenerator is determined by the rate at which air is supplied, and this will

normally match the rate at which sulphur is acquired by the gasifier. The effect of increasing the flow rate of bed material will be to reduce its sulphur content and hence the amount of heat generated within the regenerator per unit weight of lime. Since the lime enters the regenerator at a temperature of 850°C and is heated to a temperature of 1050°C there must clearly be a specific bed transfer rate for any particular set of operating conditions at which the regenerator temperature is in equilibrium at the desired level. It follows from this that an accurate and reliable method for controlling bed transfer rates is an essential requirement for successful operation. The method which has been chosen is gravitational dense phase transfer. Each bed container is provided with a catchment pocket slightly above the surface of the bed, and each of these pockets communicates via an almost vertical duct with the side wall of its neighbour at a point slightly above the level of the distributor. There is a short horizontal section at the bottom of each duct so that in the absence of any external stimulus the two transfer ducts simply fill with static bed material. An arrangement of this type is shown in Figure 8 which gives a schematic layout of the first bed transfer test rig.

TEST RIG FOR BED TRANSFER TRIALS

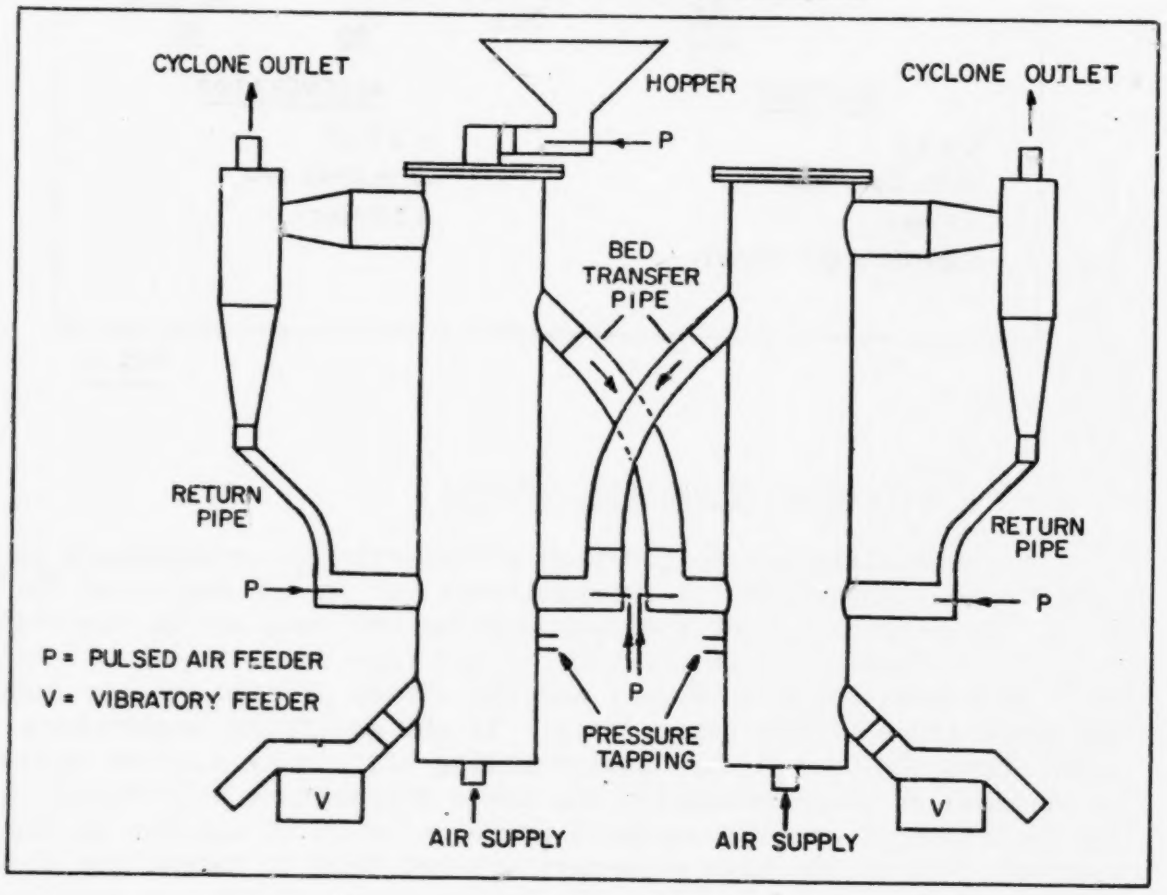


FIGURE 8

Each horizontal connection is provided with a suitable tube running parallel with its axis. When gas is introduced via one of these tubes the particles in the horizontal duct are fluidised and expelled, being replaced by gravitational flow down the vertical duct. As soon as the gas ceases to flow so do the solids. By pulsing the gas flow and varying the frequency of the pulses it is possible to closely con-

trol the rate at which bed material is transferred. Very little gas is required to operate the system. In the original test rig it was possible to shift about two pounds of bed material per cubic foot of gas. In view of the possible variation of sulphur content throughout the depth of the bed, the transfer of material from the top of each bed to the bottom of the other is advantageous from an operational point of view. The dense packing in each duct, together with the continuous gas bleed which is required to prevent blockage of the activating tubes, ensures that the leakage of gas between compartments is minimal.

(d) The Detailed Design of the Bed Transfer System

The layout of the bed transfer ducts was largely dictated by the geometry of the gasifing and regenerating compartments. It was not possible, however, to produce a detailed design on theoretical grounds. There was no way of predicting the dimensions and positions of the catchment pockets which would provide satisfactory results for example, and it would have required an excessive degree of confidence in the outcome to have simply guessed the dimensions of the transfer ducts. It was, therefore, decided at an early stage that the best procedure would be to build a full scale cold model so that these finer points could be settled experimentally. A view of the cold model is shown in Figure 9.

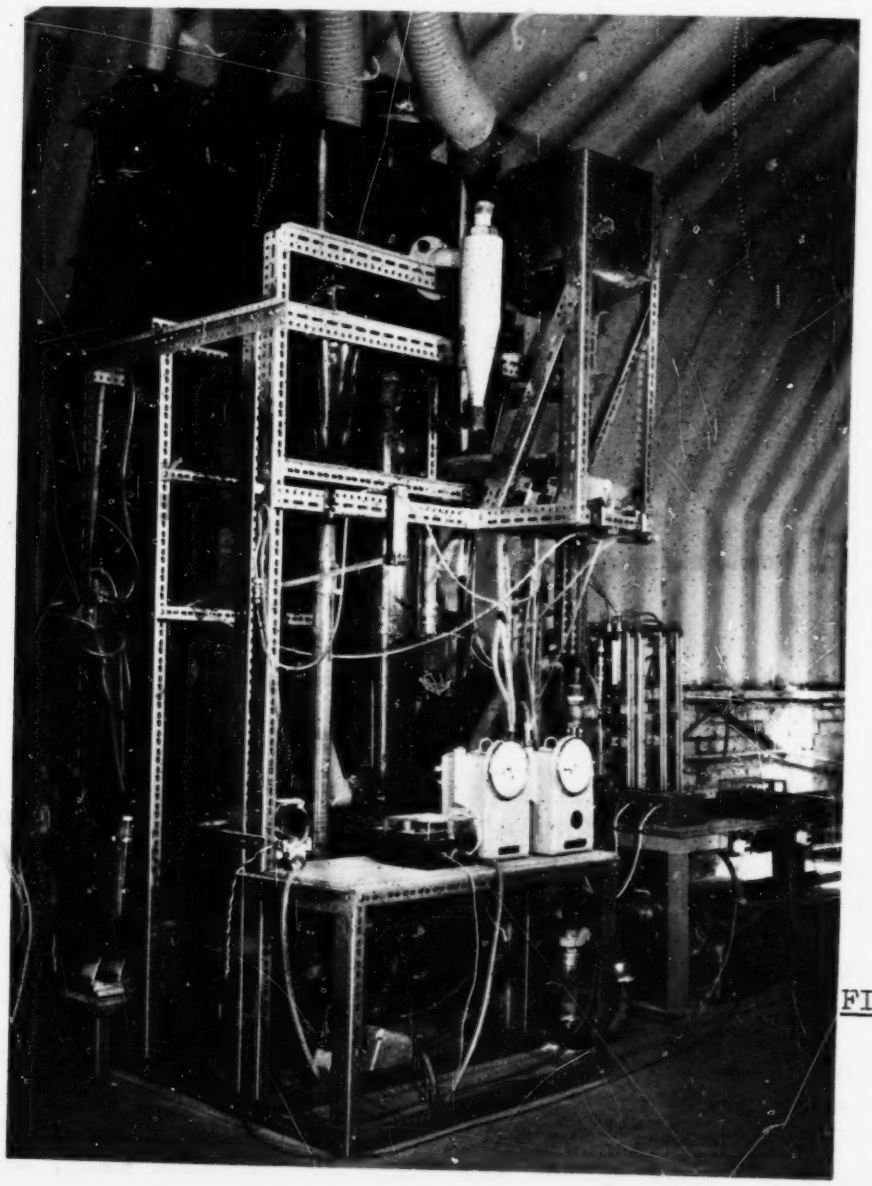


FIGURE 9

The greater part of the structure was constructed of thin steel sheet, but the bed transfer system was made of transparent plastic so that the behaviour of the flowing solids could be observed. Plastic construction also lent itself to rapid modification.

The bed material which was used to test the cold model was a crushed brick having the same size distribution and bulk density as the lime which was normally used in the batch units.

Trouble was in fact encountered with the original design in which the fines from the main cyclones were led directly into the bed transfer ducts through branch pipes. It was found that the prevailing flow of gas up the transfer ducts from the gas injectors carried fines into the interstices between the coarser material up stream of the cyclone branches and that this resulted in bridging. This difficulty was overcome by adopting the configuration shown in Figure 10.

SUCCESSFUL CYCLONE FINES RETURN ZONE

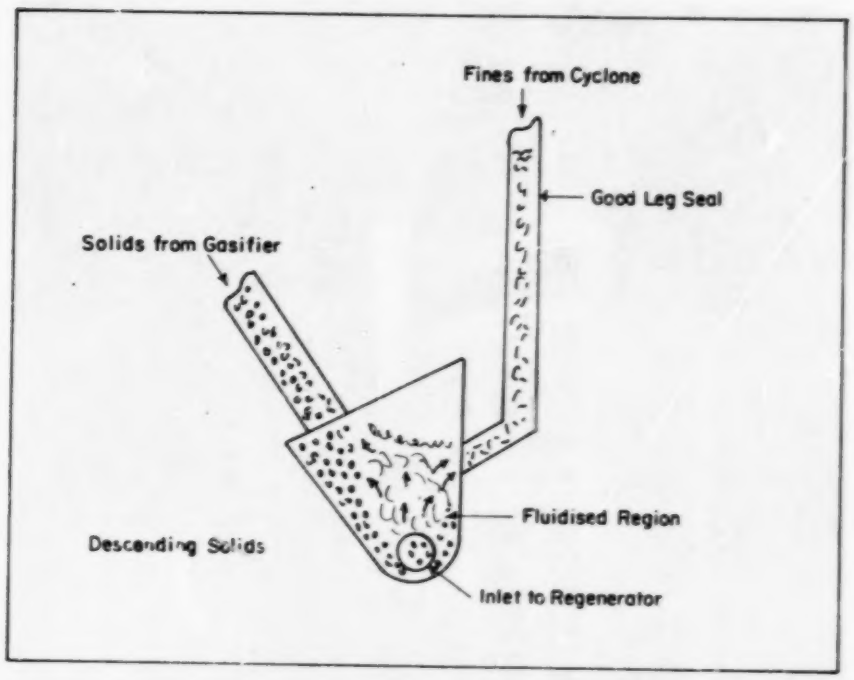


FIG. 10.

The transfer duct was enlarged at the point at which it changed direction horizontally to form a chamber having a vertical face which was swept by gas bubbles rising from the injector. The shape of this chamber was such that a free surface of bed material existed within it, so that the gas bubbling up the verticle face could only continue on up the duct by re-entering this surface which therefore acted as a trap for fines.

The fines from the cyclone entered the entrainment chamber through its bubble swept face, and the mouth of the duct from which they drained was positioned so that it was partially open to the voidage above the free bed surface. This system was found to function well, and it was

possible to observe entrained pockets of fines being carried towards the delivery port by the coarser bed material.

The behaviour of the system is likely to vary with the temperature at which it is operated. For example the volume of the activating gas will increase by a factor of four at the normal running temperature of the gasifier whilst the viscosity of the gas will also be increased. Both of these trends are in a favourable direction. Consequently the satisfactory operation of the cold rig indicates a high probability of success of the gasifier.

It is intended to check the operation of the transfer system of the gasifier under cold conditions and to compare the results with those obtained from the test rig in order to establish whether or not the transfer ducts are free from obstructions.

(e) Bed Transfer Control Loop

The bed transfer system, which is used to control the temperature of the regenerator bed, lends itself readily to automatic control. It was decided to install a controller in order to reduce the manning requirements of the experimental installation.

In the control system which has been adopted the process timer controlling the transfer of material from the gasifier bed to the regenerator bed is operated by the signal from a thermocouple in the regenerator. When the temperature rises above 1050°C the bed transfer rate is increased, when the temperature drops below 1050°C the transfer rate is decreased. The return flow from the regenerator to the gasifier is controlled by a pressure switch which actuates this transfer line at a predetermined depth of bed, and inactivates it at a lower level. By measuring the rate at which the depth of the regenerator bed increases between activations of the return line it is possible to estimate the rate of bed transfer under operating conditions. Since bed depth is measured in terms of pressure drop the result is given directly in terms of weight transferred. This control loop, minus the thermocouple, has been tested on the cold unit and has been found to operate in a satisfactory fashion.

(f) Gasifier Construction

Construction of the gasifier unit itself consisted of bolting together the base and prelined steel sides, building up the cores and molds which form the interior voids, pouring the refractory concrete interior and assembling the lids and distributors.

The base is mounted on concrete piers in a pit which houses the gasifier unit. The eight side plates have a layer 3-inch thick of 50 lb/cu. ft insulating castable which was cast in place on the ground before erection. All penetrations through the walls had been precast in this insulating concrete. The bottom four side sections were assembled on the base and lined with a $\frac{1}{4}$-inch thick blanket of expanded polystyrene sheet to provide the expansion gap. The wooden lower sections of gasifier and regenerator cores were set in place along with plexiglas cores for the transfer lines and catch pockets. The plastic sections were filled with paraffin wax to provide rigidity. The metal inserts for fuel

injection, thermocouples, pressure taps, sampling etc. were installed and grease coated to provide for easy removal.

The first three lifts of refractory concrete were then poured. The material was G.R. Stein C-1600 high strength concrete poured and vibrated to maximum density. When the first lifts had set, the upper four side plates were bolted into place, polystyrene blankets, upper cores and inserts placed, and the final three lifts of concrete poured. Precast concrete forms were used in the start-up burner entrance, for the regenerator outlet section, and for the cyclone outlets. Stainless steel inserts formed the cyclone outlet tubes. Final assembly steps consisted of pouring a layer of insulating cement on the top, seating the precast lid, installation of refractory fibre packing in the joints, and bolting on the cover plate.

(g) Completion Schedule

Although major elements of equipment are now in place for the gasifier pilot plant, a considerable amount of hook-up and pre-start up work remains. Major target dates on the schedule are listed below.

Complete gasifier assembly	February 5th
Fire-in gasifier	February 20th - March 6th
Cold Running Tests	March 13th - 17th
Operation hot as combustor	April 10th - 24th
Install burner on boiler	May 1st
Ready for operation as gasifier	May 15th

C. Results and Discussion

Experimental results on the CA'B gasification and regeneration reactions were obtained in batch reactors described in Part II B. Studies of an engineering nature were conducted in the cold model of the continuous gasifier. Tests were also performed on experimental burners to devise means of combusting the gasifier product.

1. Batch Reactor Studies

In general, batch reactor studies consisted either of fresh bed tests or of multicycle tests with partial lime replacement between cycles. Temperature and concentrations of reaction products during regeneration were measured.

(a) Fresh Bed Tests

The first series of tests conducted in the tall (9 ft. reaction section) batch reactor at 4 ft/sec. superficial air rate without underfiring produced much better desulphurisation efficiency at low air/fuel ratio than had been obtained previously. The previous tests had used air rates from 1 to 2 ft/sec. and had required underfiring to avoid rapid laydown of heavy coke deposits in the bed. Figure A-6 of Appendix A shows curves of sulphur removal efficiency versus fraction

of calcium reacted for these tests. Except for the case of the lowest (20.7% of stoichiometric) air fuel ratio, the lime beds maintained sulphur pick-up efficiency of better than 97.5% to calcium utilisation levels of 15%. However, the 20.7% run showed an immediate decline to about 65% efficiency.

Subsequent to this series of five runs, operations were shifted to the modified 1-A reactor which has the same reactor diameter as the tall unit but which is only 33 inches high between its distributor and the entrance to the expanded section. Results obtained in fresh bed tests with the short reactor, though much better than the low velocity results with underfiring, have not matched the high performance of the tall unit at air/fuel ratios between 21 and 25% of stoichiometric.

Most of the fresh bed tests made during this study have been attempts to reproduce the high efficiencies found earlier and to understand the differences in results observed between similar tests.

Figure 11 summarises the results of the fresh bed studies. It is a plot of sulphur removal efficiency at 10% calcium reacted (designated E_{10}) versus the percent of stoichiometric air/fuel ratio used in the test.

The table below shows the legend used in Figures 11, 12 and 13.

Symbol	Injector	Distributor P	Reactor	Lime	Fuel
◊	Short	Low	Tall	UK	UK
△	Centre	Low	Short	UK	UK
▲	Centre	Low	Short	UK	US
○	Short	Low	Short	UK	UK
●	Short	High	Short	UK	UK
+	Short	Low	Short	US 1691	UK
×	Short	Low	Short	US 1690	UK
□	Short	High	Short	US 1691	US

Slashes denote period of cracked reactor lining.

VARIATION OF SULPHUR RECOVERY WITH AIR/FUEL RATIO

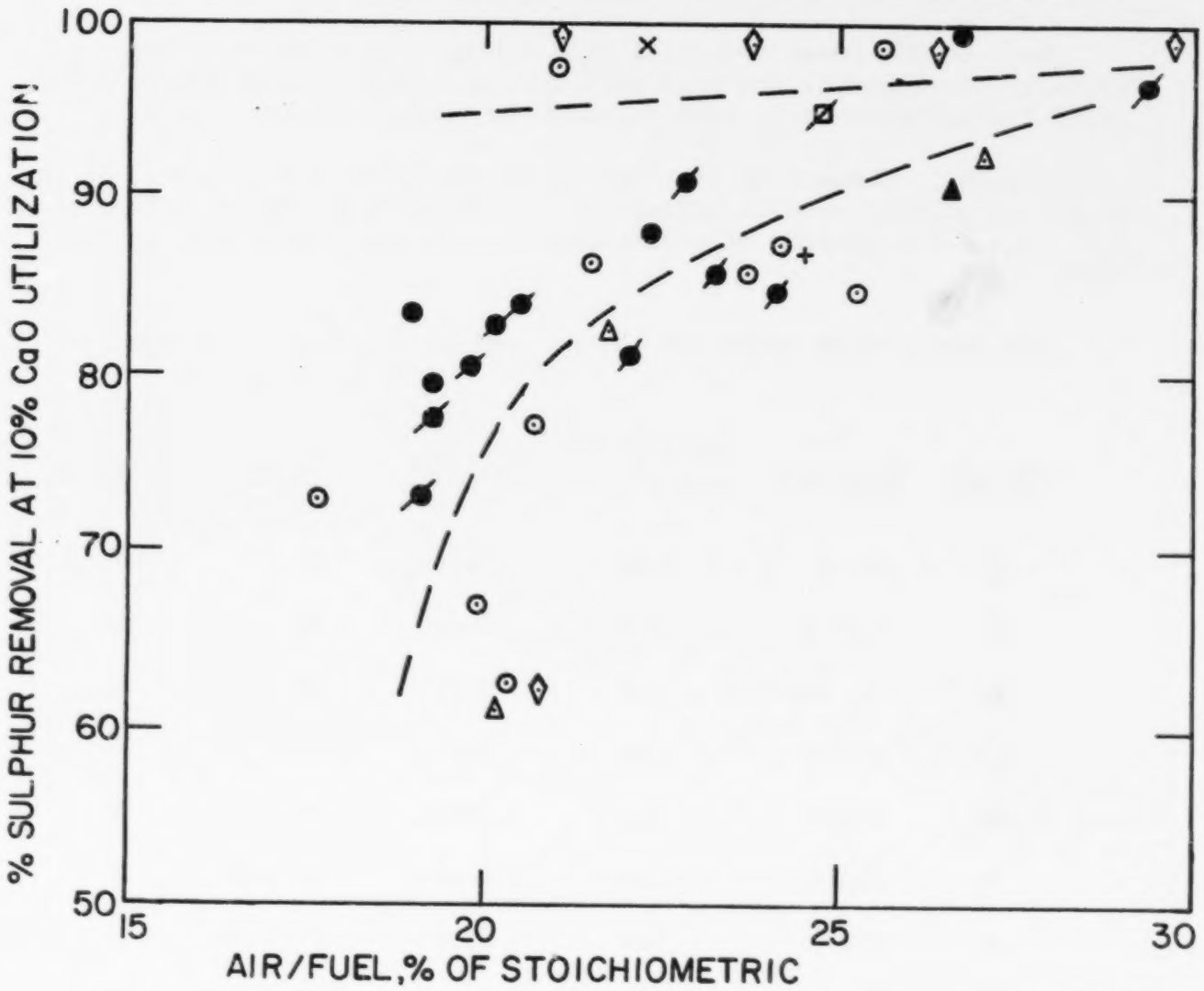


FIG. 11.

For simplicity in discussing the results, the data in Figure 11 have been separated into three categories of sulphur removal quality, designated as excellent, average and poor. These arbitrary classes are indicated by the dashed curves drawn in Figure 11 between groups of points.

(1) Effect of Air/Fuel Ratio

Except for the group of points in the excellent category, the data show a decline in sulphur pick-up efficiency as air/fuel ratio is reduced. Such a decline would be expected on theoretical grounds, since reduction of air available for combustion would tend to reduce the rate of carbon burn-off from the lime particles and could lead to local cooling with poor oil distribution in the vicinity of the oil injector. Heat balance calculations show that, under adiabatic conditions, 15% of stoichiometric air is the minimum at which 850°C could be maintained. Since our reactor loses heat through its walls, its minimum operable air/fuel ratio must be somewhat higher than this theoretical value. While the decrease in availability of heat can explain the general decline in sulphur removal efficiency with decreasing air/fuel ratio, other factors must be responsible for differences observed between experiments at roughly the same air fuel ratios.

(2) Carbon on Stone

As air/fuel ratio is reduced below about 25% of stoichiometric the quantity of carbon formed in the bed increases rapidly. Figure 12 shows the relationship observed. Values of average carbon formation rate were estimated from carbon oxide content of the gas made during the early portion of regeneration.

Although it is reasonable to expect that carbon on the lime would interfere with sulphur pick-up, Figure 13 shows that carbon formation accounts for only part of the variation observed in desulphurising efficiency. This figure is a cross plot of data from Figures 11 and 12 which shows the change of E_{10} with carbon formation rate. Distributor design appears to influence this relationship because at equal carbon rates, the high pressure drop distributor shows better efficiency. Data from the lower pressure drop distributor show greater variability.

(3) Fluidisation Variables

A number of factors have been varied in seeking the cause of differences in desulphurising efficiency and carbon formation at nominally similar conditions. None have as yet been found which can completely account for the differences, but fuel injector nozzle location and distributor design appear to be important factors.

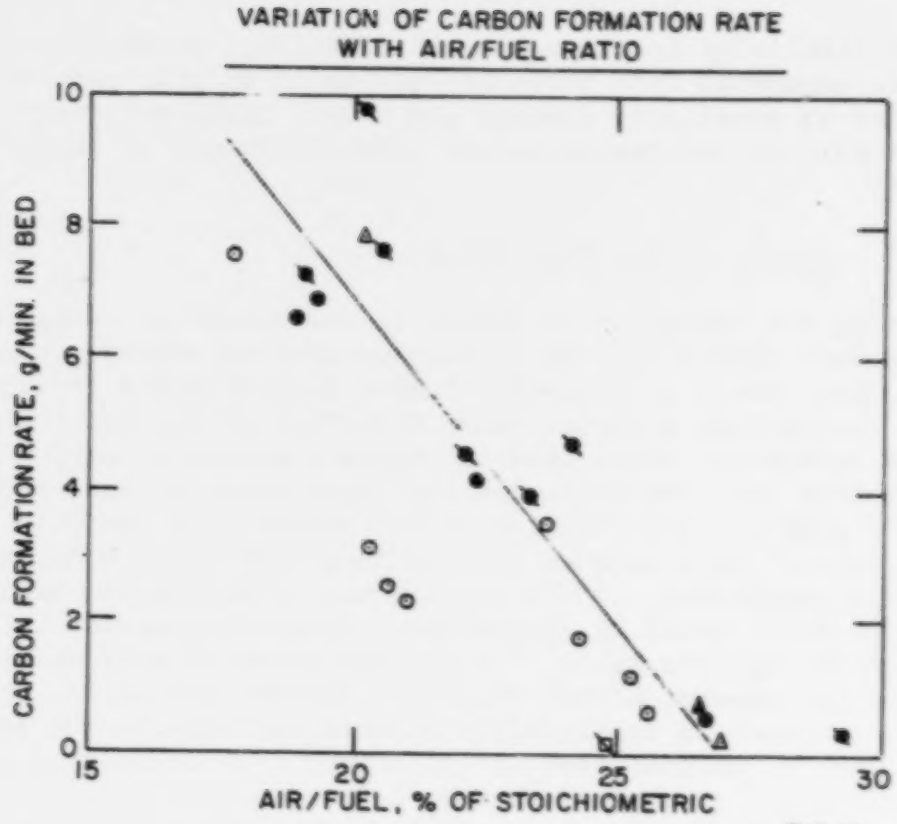

VARIATION OF CARBON FORMATION RATE
WITH AIR/FUEL RATIO
CARBON FORMATION RATE, g/MIN. IN BED
AIR/FUEL, % OF STOICHIOMETRIC
0
2
4
6
8
10
15
20
25
30

FIG. 12.

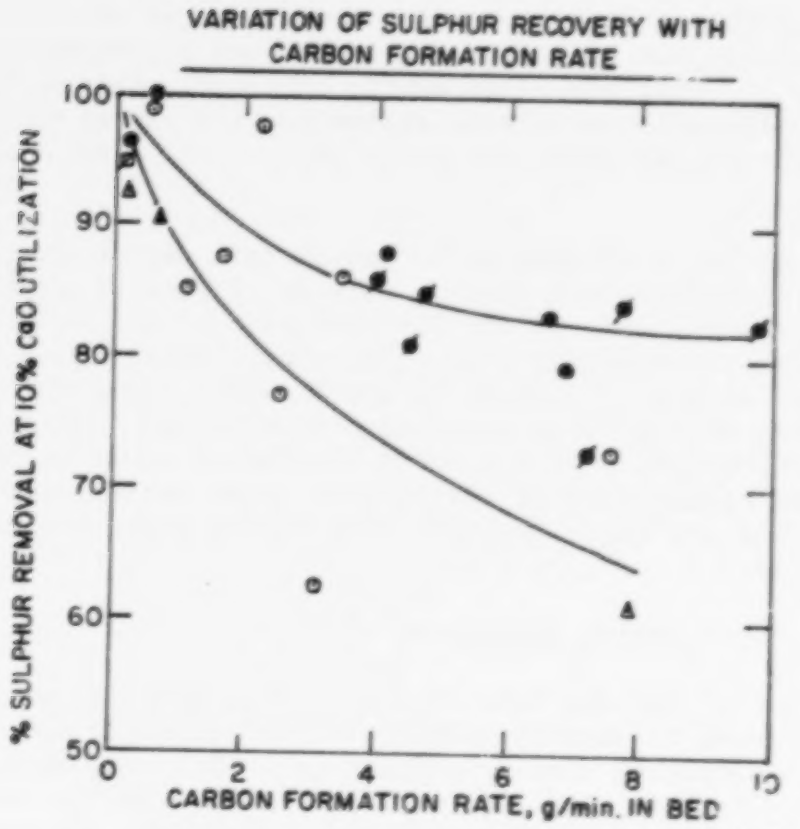

VARIATION OF SULPHUR RECOVERY WITH
CARBON FORMATION RATE
% SULPHUR REMOVAL AT 10% CaO UTILIZATION
CARBON FORMATION RATE, g/min. IN BED
50
60
70
80
90
100
0
2
4
6
8
10

FIG. 13.

Fuel Injector

Four runs made with a fuel injector extended to the centre of the reactor gave results in the poor category. This result is attributed to incomplete fluidisation in the poorly aerated region just above the centre of the top hat distributor. Relocation of the injector to a position above the annular region between wall and distributor has improved the average but not eliminated the occasional poor result.

Air Injected with Fuel

To improve fuel distribution and help cool the injector, a small stream of air is passed through the injector along with the fuel. The normal rate is one CFM. Tests with used lime beds were made in which this rate was varied from 0.5 to 1.5 CFM. As judged by the quantity of carbon laydown in the bed, the variation in air injection had no effect.

Run No.	Stoichiometric Air %	Air Injected with Fuel	Carbon Formation Rate, gm/min
28-a	21.3	1	.73
28-b	21.1	1.5	1.01
28-c	19.3	0.5	1.44

Distributor Design

In Figure 11, most of the tests made with a higher pressure drop distributor gave desulphurisation results in the average category, with only 3 of 14 falling in the poor group. Six out of ten tests with the low pressure drop distributor fell in the poor group. This distributor also showed greater variability, as it gave two runs in the excellent group. The high pressure drop distributor tended to produce higher carbon formation rates, but as noted above, it tended to give better desulphurisation in spite of the carbon.

Temperatures

The effect of temperature had been studied early in the CAFB programme at air/fuel ratios above 30% of stoichiometric with results indicating no effect of temperature on desulphurising efficiency in the range of 800-900°C. Consequently, no temperature control system was installed in batch reactor 1-A. The reactor insulation was adjusted to give a rate of heat loss which allowed operation in the 800-900°C range with air/fuel ratios between 20 and 30% of stoichiometric. With this arrangement the temperature tends to vary with fuel rate, and most of the low air/fuel ratio runs operate in the lower portion of the temperature range.

Within the range of data available, there is no correlation between sulphur absorption efficiency and temperature. However, because of the cross correlation between temperature and air/fuel ratio the temperature-efficiency correlation could be

missed. We plan to investigate this factor again with the new batch units which will have a temperature control system to permit independent variation of temperature and air/fuel ratio.

Superficial Air Rate

Air velocity has been held at about 4 ft/sec. (at operating temperature in empty bed) in most of the tests to date. One test at the higher velocity of 4.8 ft/sec. indicates that sulphur removal efficiency remained constant over this range of velocities. The results (of runs at near identical conditions other than velocity) are compared in curves of sulphur removal vs. CaO utilisation in Figure 14. There was some increase in lime loss at the higher velocity; about 750 g lost at 4.8 ft/sec in 90 minutes compared with 550 g at 1.9 ft/sec in a 120 minute run.

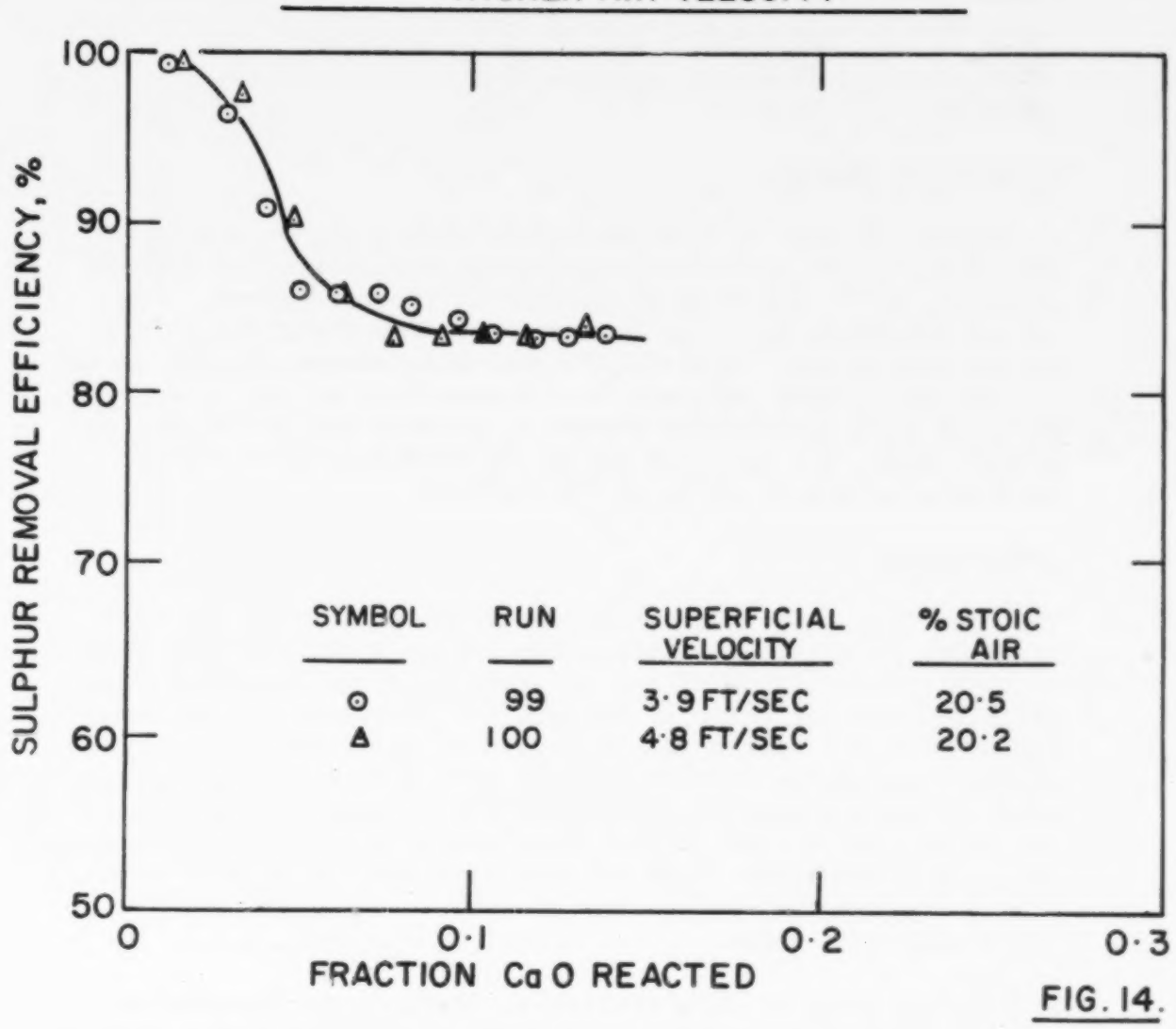


FIG. 14.

(4) US Fuel Oil

The majority of fresh bed tests were made with the UK fuel oil containing 3.03% sulphur. An early test was made to compare the performance of the US fuel oil supplied by APCO with this UK standard. Results are shown in Figure 15. The comparison tests were made at approximately 27% of stoichiometric air using the centre injection nozzle. Figure 15 shows nearly identical behaviour for the two fuels when compared on the basis of equal sulphur pick-up. Of course the US fuel takes longer to build up an equal sulphur content on the lime since it contains only 2/3 the concentration of sulphur.

On the basis of this test, the US fuel sample was judged to be satisfactory for CAFB operations and a large supply was ordered for an intensive variable study.

SULPHUR REMOVAL COMPARISON FOR U.S. AND U.K FUELS

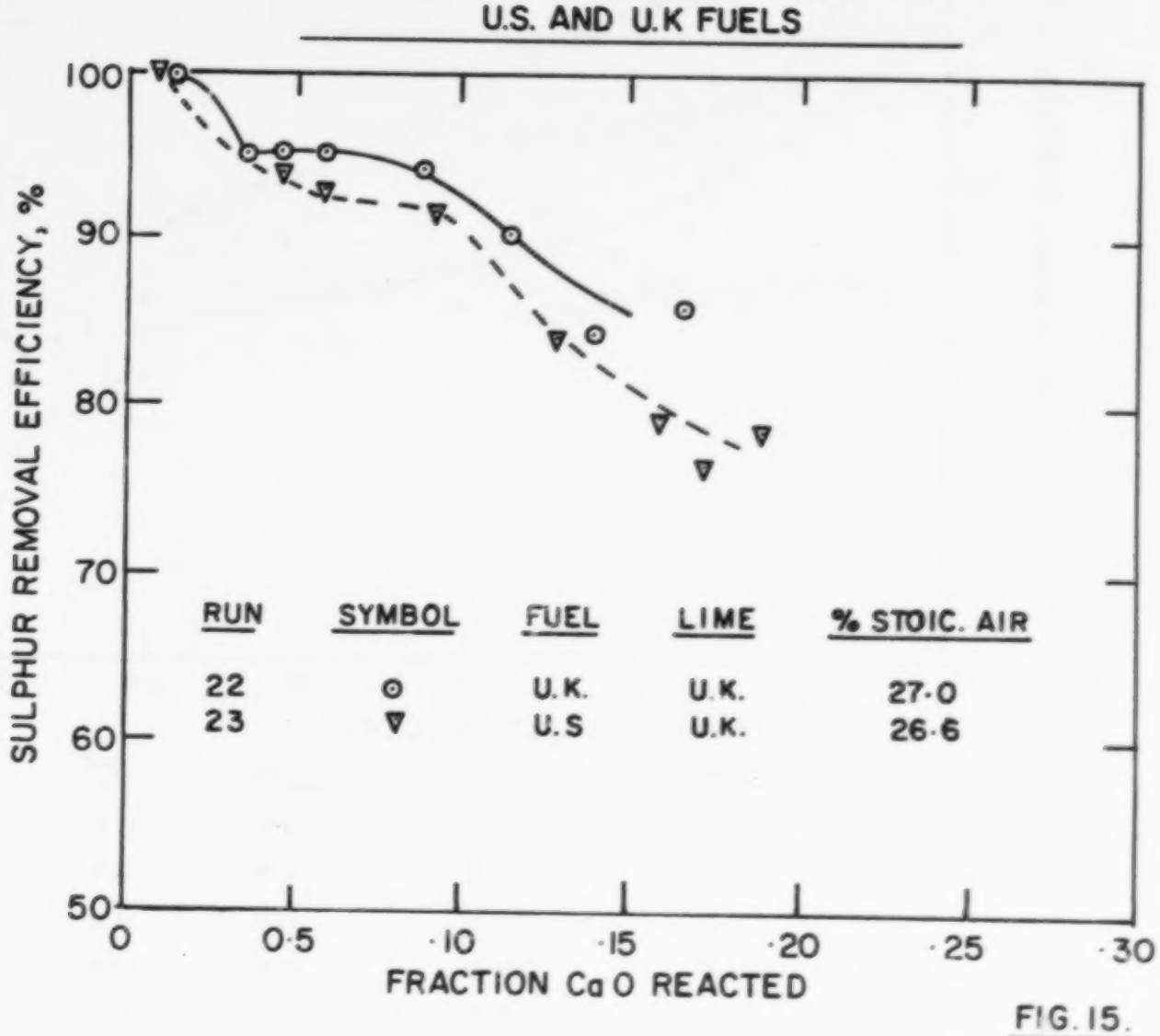
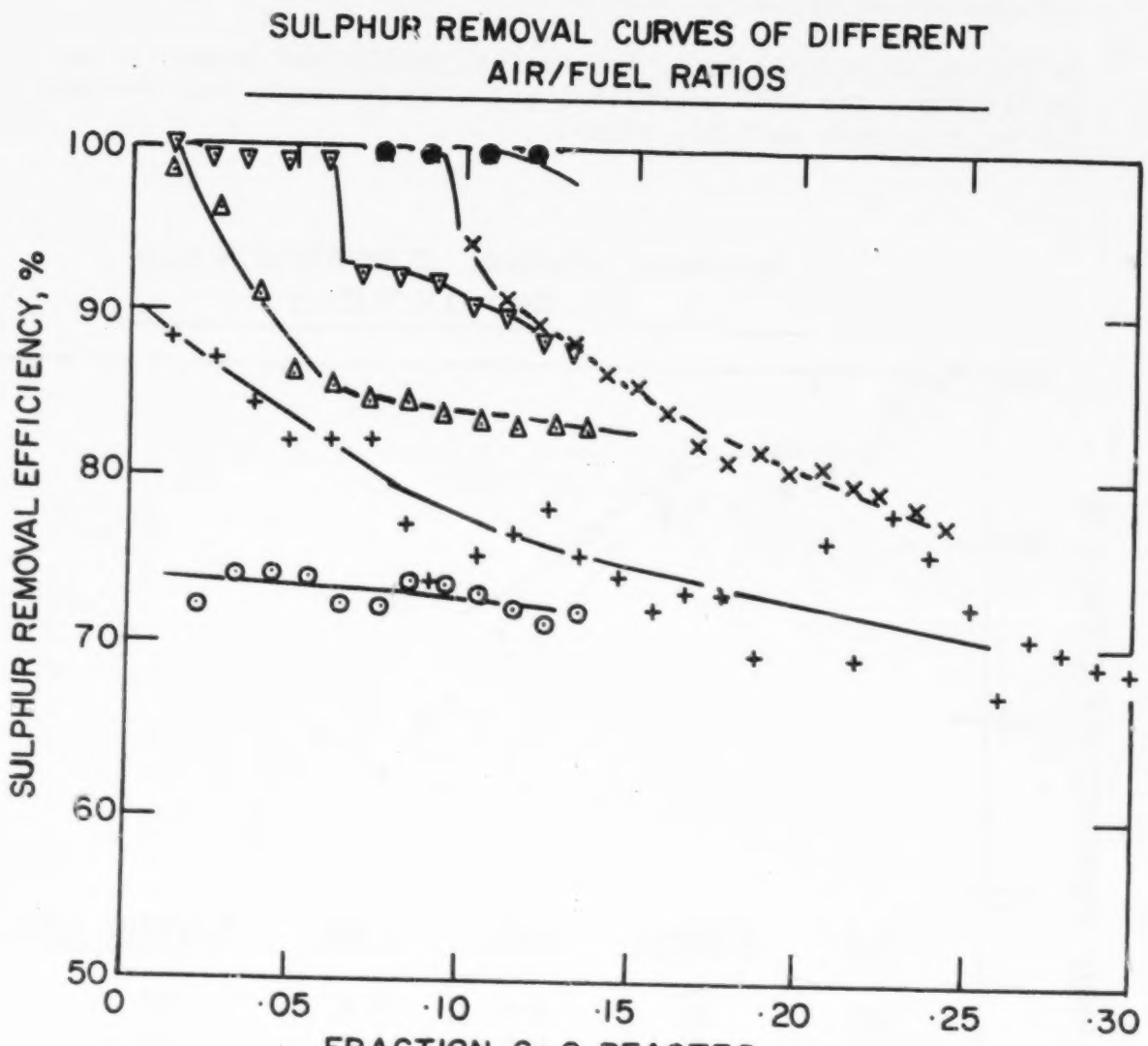


FIG. 15.

(5) Variation of Efficiency with Lime Utilisation

As air fuel ratio and other factors changed, the manner in which sulphur removal efficiency varied with lime utilisation also changed. Figure 16 shows selected curves for several air/fuel ratios which best illustrate this variation. At low air/fuel ratio, the efficiency fell almost at once to a low level and then tended to level out. At intermediate conditions the sulphur pick-up was complete for a brief period but then fell rapidly before levelling out. As conditions improved the period of complete sulphur pick-up increased and the loss in efficiency which eventually occurred was not as rapid.



RUN	SYMBOL	% STOIC AIR	FUEL	LIME
98	⊙	19·1	U.K.	U.K.
96	+	19·3	U.K.	U.K.
99	△	20·5	U.K.	U.K
102	▽	22·8	U.K.	U.K.
103	×	24·8	U.S.	U.S.
121	●	26·7	U.K.	U.K

FIG. 16.

(6) US Fuel and Lime

Figure 16 includes data (shown by +) from run 103 made with the US fuel oil sample and limestone 1691. Data from this run fit in quite well with the others when the comparison is made on an equal lime utilisation basis.

Nearly 100% sulphur removal efficiency was maintained up to a CaO utilisation of 9%.

(7) Bed Processes during Gasification

The chemical processes taking place in the CAFB gasifier are a complicated mixture of cracking, coking, oxidation, absorption and gasification. Oil enters the bed some distance above the air distributor where little or no oxygen is present. The oil contacts hot lime particles, is partly vaporised, and undergoes cracking and coking. Most of the sulphur is probably evolved as H_2S and absorbed higher in the bed. The lime particles, coated with carbon and heavy hydrocarbon, return to the region of the air distributor, where the layer of coke is oxidised. This oxidation supplies heat to the system and removes the carbon barrier to further absorption. The temperature of lime particles in the vicinity of the distributor may be high enough to convert some of the calcium sulphide to sulphate or even to oxidise the sulphide to SO_2 and CaO. In the latter case, the SO_2 would be reabsorbed higher in the bed.

The shape of the reaction curves in Figure 16 indicate that several resistances may play a part in determining the reaction rate under different conditions or at different stages in a cycle. At low air/fuel ratios there is probably insufficient air to remove the carbon as fast as it is deposited on the lime, and there is a rapid build-up of carbon early in the cycle. The fact that efficiency tends to line out after a period indicates that carbon does not build-up continuously but eventually reaches a constant level. This implies that carbon burn off rate increases with carbon concentration in the bed until burn off rate equals formation rate.

At higher air/fuel ratio the carbon formation rate is not as high, and for a period the lime absorbs all of the sulphur being fed. The increasing carbon concentration eventually interferes with sulphur absorption rate, and efficiency falls. Eventually the carbon formation is matched by burn off rate and efficiency levels off.

At sufficiently high air/fuel ratios carbon formation never presents an absorption barrier, and efficiency remains high until the decreasing concentration of CaO in the products of reaction becomes the controlling resistance.

(b) Regeneration

After each gasification test a regeneration was effected by cutting off the fuel, continuing the air flow and allowing the temperature to rise. Temperature and gas composition were monitored during the regeneration cycle. Figure 17 shows behaviour of a typical regeneration (this particular run was made with the US fuel and limestone 1691). There is an initial period of high CO_2 evolution as carbon is burned off the lime, and the temperature rises. SO_2 concentration then increases and reaches a maximum at temperatures near 1050°C. Then as the reaction with CaS nears completion oxygen begins to break through, and CO_2 again appears as carbon deposited higher in the reactor is burned. Finally the temperature falls, and the system is ready for another gasification.

REGENERATION OF U.S. LIMESTONE (1691)

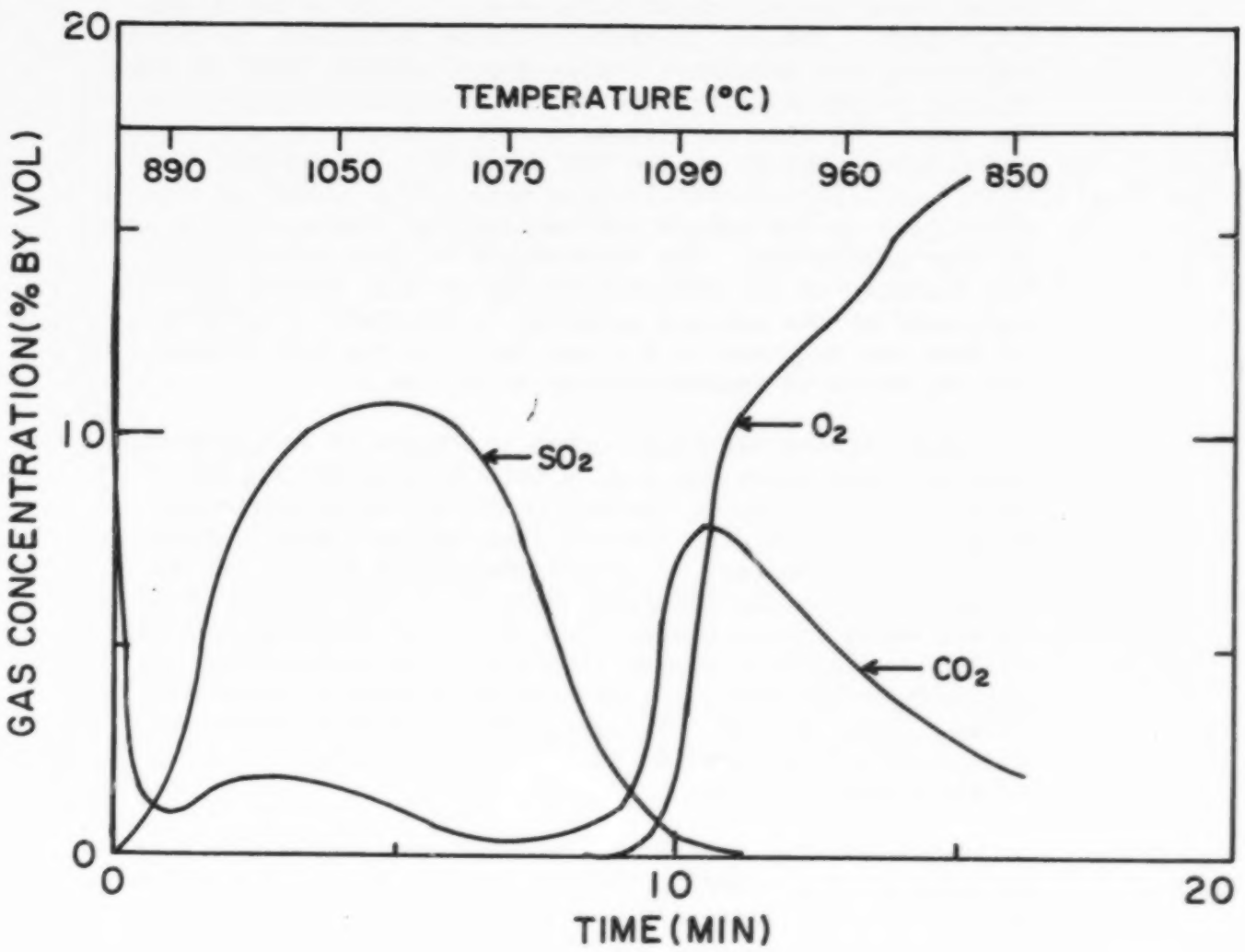


FIGURE 17

Following gasification runs in which a large amount of carbon was deposited, the period of high CO_2 evolution lasted much longer than shown in the example. The quantity of CO_2 and CO evolved during regeneration provided a measure of carbon laid down during gasification.

The fact that oxygen breakthrough does not take place until nearly all of the CaS has been reacted means that the rate is high enough at low CaS and O_2 concentrations to permit continuous regenerator operation with little excess air. Provided that carbon content of the lime from the gasifier is low, there should be little difficulty in producing 10% or higher concentrations of SO_2 in the regenerator off gas from a continuous unit.

(c) Cyclic Batch Tests

When successive cycles of gasification and regeneration are repeated, the sulphur absorption efficiency, at a given lime utilisation, falls for several cycles and then lines out. A portion of the bed must be replaced after each cycle to make up losses due to attrition and sampling; the greater the replacement fraction, the higher is the lined out level of sulphur absorption efficiency. The Appendix figure A-1 shows behaviour through 20 cycles of gasification-regeneration in a low velocity unit with underfiring. At a replacement ratio of 0.5 wt. CaO/wt. S the efficiency stabilised at 60% sulphur recovery. Tests at other replacement ratios showed (Figure A-2) that nearly 100% recovery could be maintained if lime replacement was 1.75 wt. CaO/wt. S or higher. These results were obtained at air/fuel ratios of 30-35% of stoichiometric and with 100 minute gasification cycles. As Figure A-7 shows, tests in the tall unit without underfiring gave essentially the same results at 25% of stoichiometric air.

As part of the check out of the 1-A unit, a 21 cycle test was made with UK fuel and the UK Denbighshire limestone. Nominal test conditions are listed below. Duration of each gasification cycle was 60 minutes.

Underfiring	None
Reagent particle size	850-1200 μ
Bed temperature for absorption	800-900°C
% stoichiometric air during absorption	25%
Superficial gas velocity	4 ft/sec
Bed depth	15.5" (18 lb lime bed)
Reagent utilisation at regeneration (% sulphur)	5%
Maximum temperature at regeneration	1100°C
Bed make-up rate	0.7% CaO/wt sulphur

If complete sulphur pick-up had been achieved the lime utilisation at the end of each cycle would have been 6.6%. The lined out efficiency after 21 cycles was actually 72% which gave lime utilisation of 4.7% per cycle. This lined out efficiency, 72% at 0.75 wt. CaO/wt. S, falls quite close to the curve established at 25% of stoichiometric air/fuel ratio in the tall unit. Figure 18 shows the cycle-efficiency curve for this test.

(1) US Limestone

The two US limestones were compared with the UK stones in cyclic tests at the same nominal conditions as far as possible. With stone 1691 a nearly direct comparison was possible. Nominal conditions were the same as listed above for the UK stone. However, to achieve the same CaO replacement rate, a higher actual stone replacement rate was required. Stone 1691 has only 81% of the CaO content of the UK stone. The cyclic efficiency curve in Figure 19 shows the same behaviour observed previously with the UK stone, and the lined out efficiency of 72% was in excellent agreement with the earlier curve.

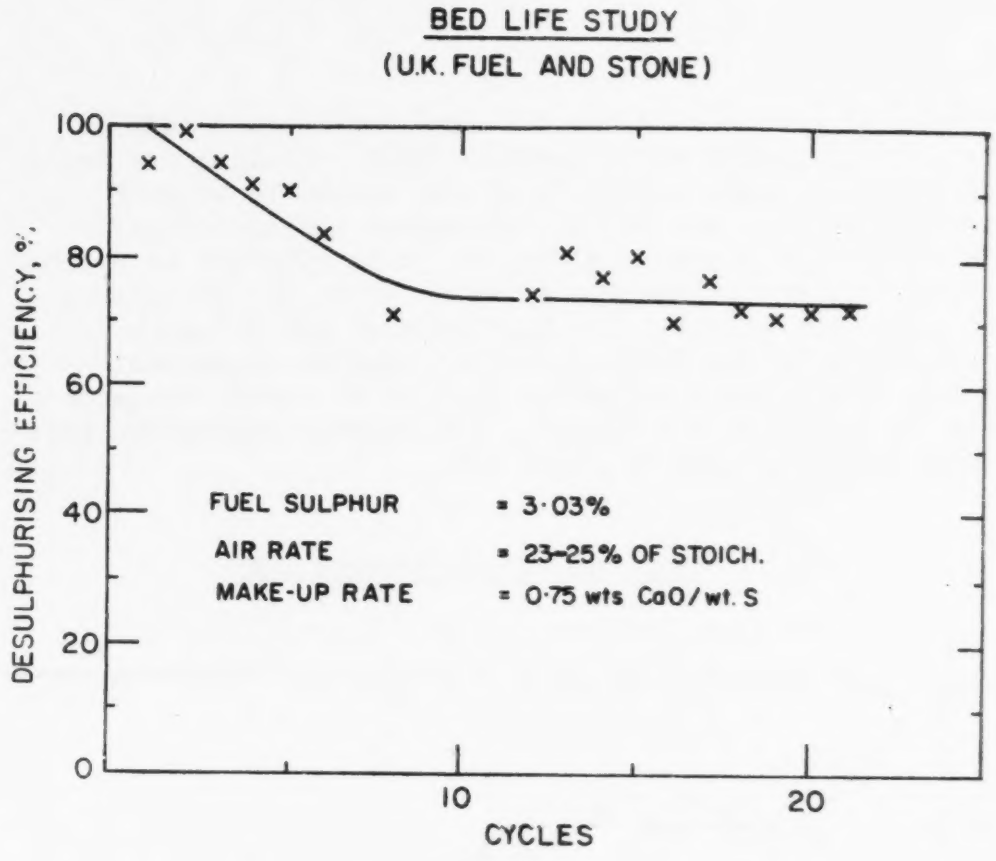


FIGURE 18

CYCLE TESTS (U.S. LIMESTONE 1691)

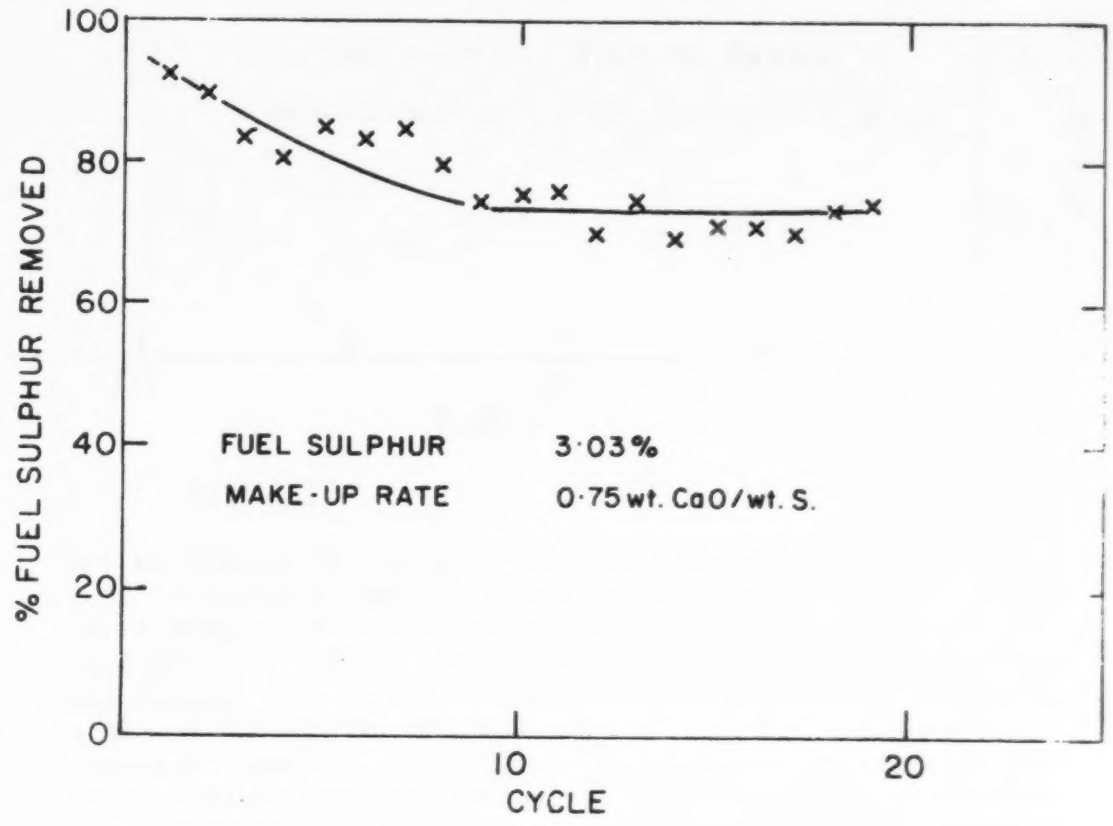


FIGURE 19

It was not possible to use the same replacement rate in the initial cycles with limestone 1690. Preliminary tests showed lime losses in the first few cycles to be much higher than 0.75 wt. CaO/S. Therefore the cyclic test was started at 1.5 wt. CaO/wt. S. This rate was maintained for ten cycles (Figure 20) by which point the efficiency has lined out at 80%. The high rate of solid losses encountered in the first cycle declined in subsequent cycles permitting a reduction to 0.75 wt. CaO/S replacement rate in the final ten cycles. The sulphur absorption efficiency then declined to about 64%.

CYCLE TESTS (U.S. LIMESTONE 1690)

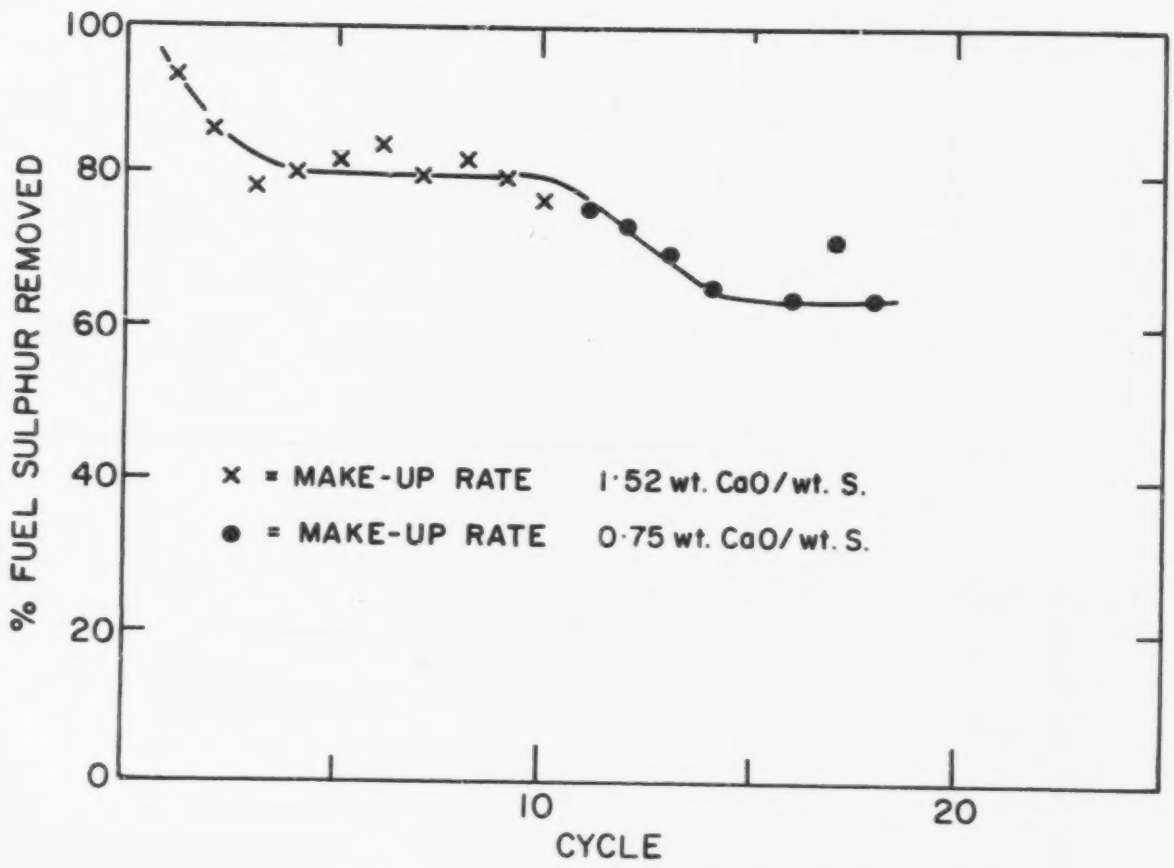


FIGURE 20

Limestone 1690 gave good sulphur removal efficiency in its first cycle, but in other respects it was inferior to 1691. Its low calcium content (60% of limestone 1691) gave it a low sulphur capacity on a total stone basis. It underwent severe attrition during calcination and in its initial gasification cycle. But even more serious, it tended to sinter and agglomerate at operating conditions. Figure 21a shows the distributor used with stone 1690 compared with a fresh distributor. Figure 21b shows some of the agglomerates. This tendency to sinter and agglomerate would present severe operating problems to a continuous CAFB unit. It has not been observed with any stone other than 1690.

COMPARISON OF DISTRIBUTORS

FIGURE 21a

AGGLOMERATES RECOVERED FROM BED

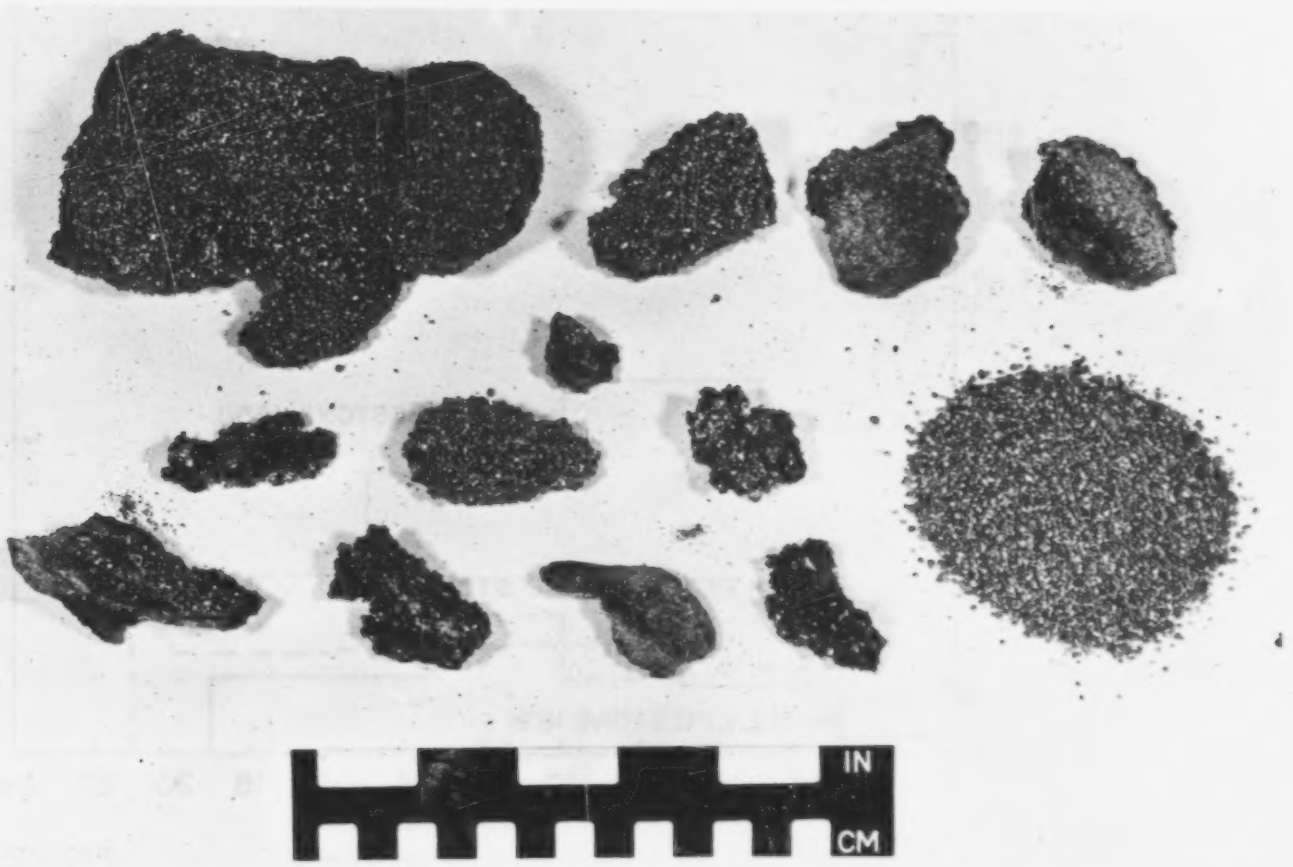


FIGURE 21b

On the basis of these cyclic tests, limestone 1691 was selected as the better of the two stones suggested by NAPCA Except for requiring a higher absolute make-up rate because of its lower CaO content, it appears to be as good as the UK Denbighshire stone for CAFB operations. On the other hand, stone 1690 does not appear very suitable for the CAFB process. It would require an even higher replacement rate, and it could cause serious operating problems.

The behaviour of US stone 1691 with the US fuel in a fresh bed test was described in Section II-C-(a)-(6) above.

(2) Lime Attrition

Lime losses during the gasification-regeneration cycles have been estimated by weighing the beds before and after the tests. In the fresh bed tests, lime losses in the single gasification-regeneration cycle averaged 6.6% of the bed, or about 2.7% of the fuel fed. In the cyclic tests, however, the losses tended to be much lower. Figure 22 shows lime losses per cycle for tests with the UK stone and the two US stones.

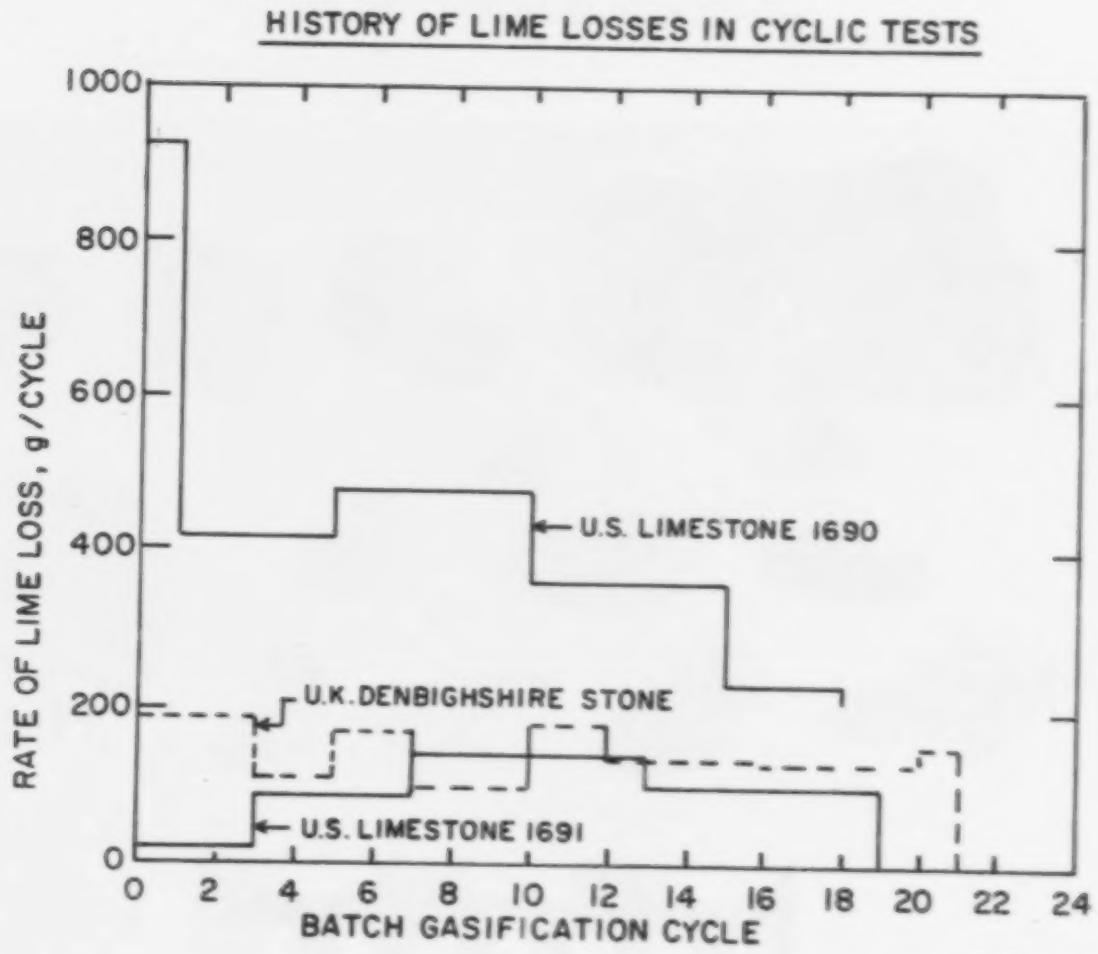


FIG. 22.

The UK stone settled down to a loss of about 140 g/cycle which was 1.7% of the bed or 1.4% on fuel fed. The US stone 1690 had a very high loss in the first cycle, but lower losses thereafter. The loss rate declined still further when replacement rate was reduced. During the final cycles the losses averaged 244 g/cycle, which is 3% of the bed or 2.5 wt. % on fuel feed rate of 165 g/min.

Losses from stone 1691 started low, increased to a maximum at about cycle 10 and then decreased again. The average rate of loss for cycles 4 through 19 was 112 g/cycle which was 1.1% of fuel feed rate.

Particle size distribution curves for the three limes during the cyclic tests are shown in Figures 23 , UK stone; 24, US 1691;and 25, US 1690. The UK stone underwent the greatest particle size change with a steady decrease in the quantity of the largest particle size range. Both US stones underwent an initial decrease in particle size, but tended to stabilise in particle size distribution after a few cycles. With both of the US stones the screen analysis indicated a small increase in the 1200-1400 micron fraction toward the end of the test series.

CHANGE IN PARTICLE SIZE DURING CYCLIC TESTS

U.K. LIME STONE

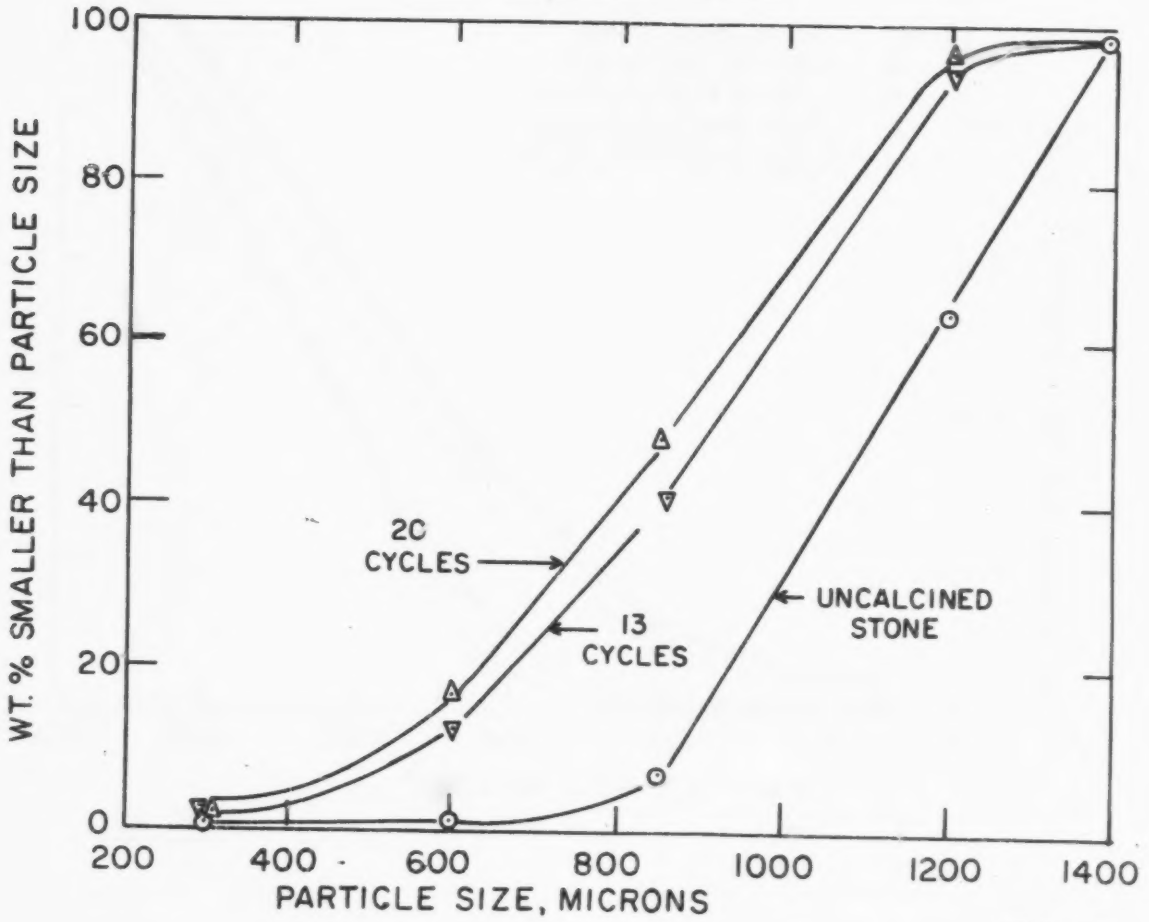


FIG. 23.

CHANGE IN PARTICLE SIZE DURING CYCLIC TESTS
U.S. LIMESTONE 1691

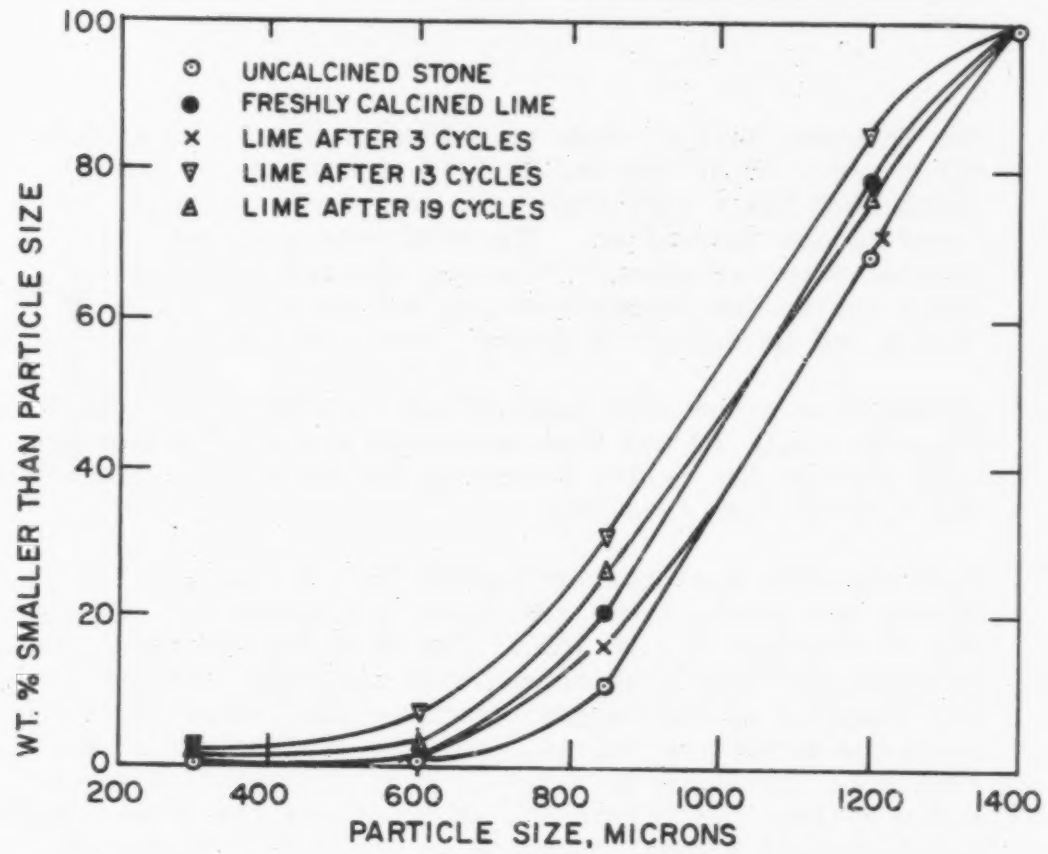


FIG. 24.

CHANGE IN PARTICLE SIZE DURING CYCLIC TESTS
U.S. LIMESTONE 1690

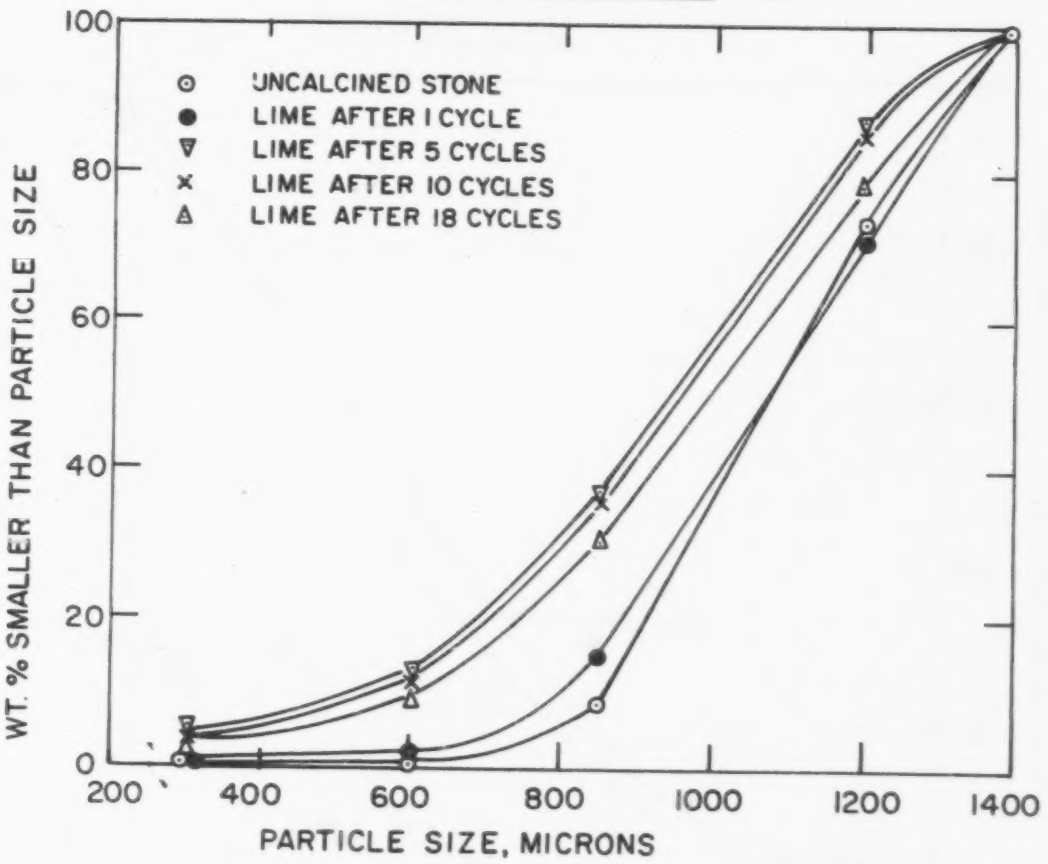


FIG. 25.

(3) Metals Removal

During the cyclic batch tests, bed samples were analysed for sodium, iron, and vanadium to determine the ability of the lime to retain metallic components of the fuel oil. Figures 26, 27 and 28 compare the observed vanadium pick-up with that predicted for 100% vanadium recovery for the UK and the two US limestones.

VANADIUM RETENTION
U.K. FUEL AND STONE

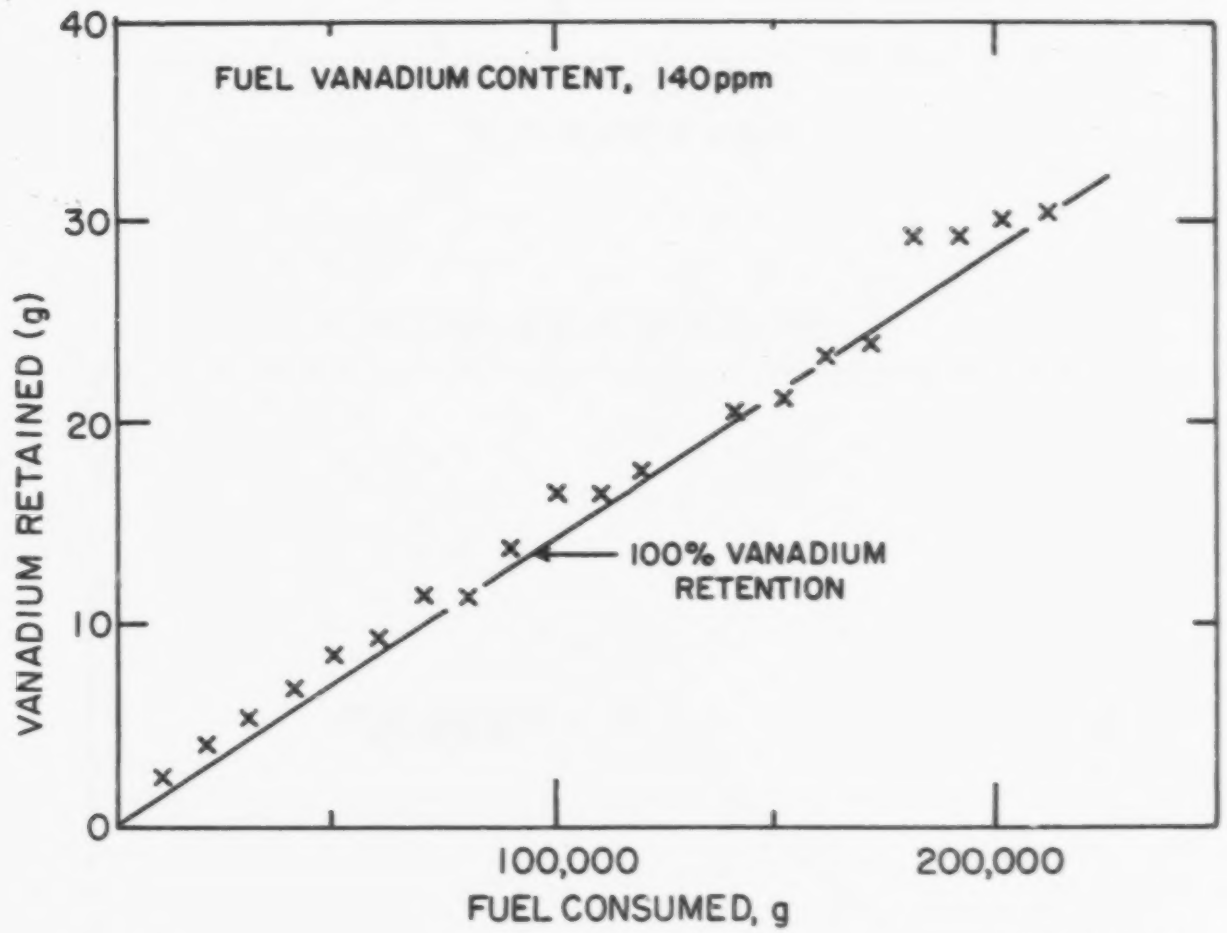


FIGURE 26

VANADIUM RETENTION (U.S. LIMESTONE 1691)

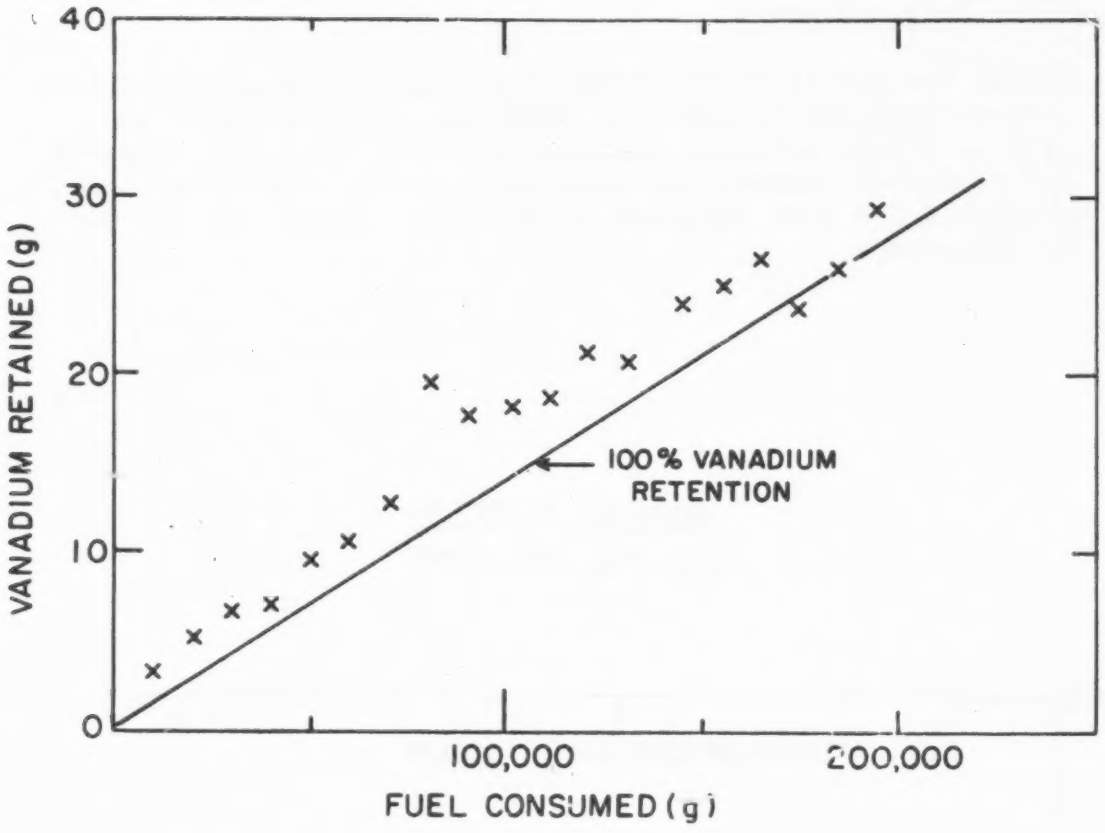


FIGURE 27

VANADIUM RETENTION (U.S. LIMESTONE 1690)

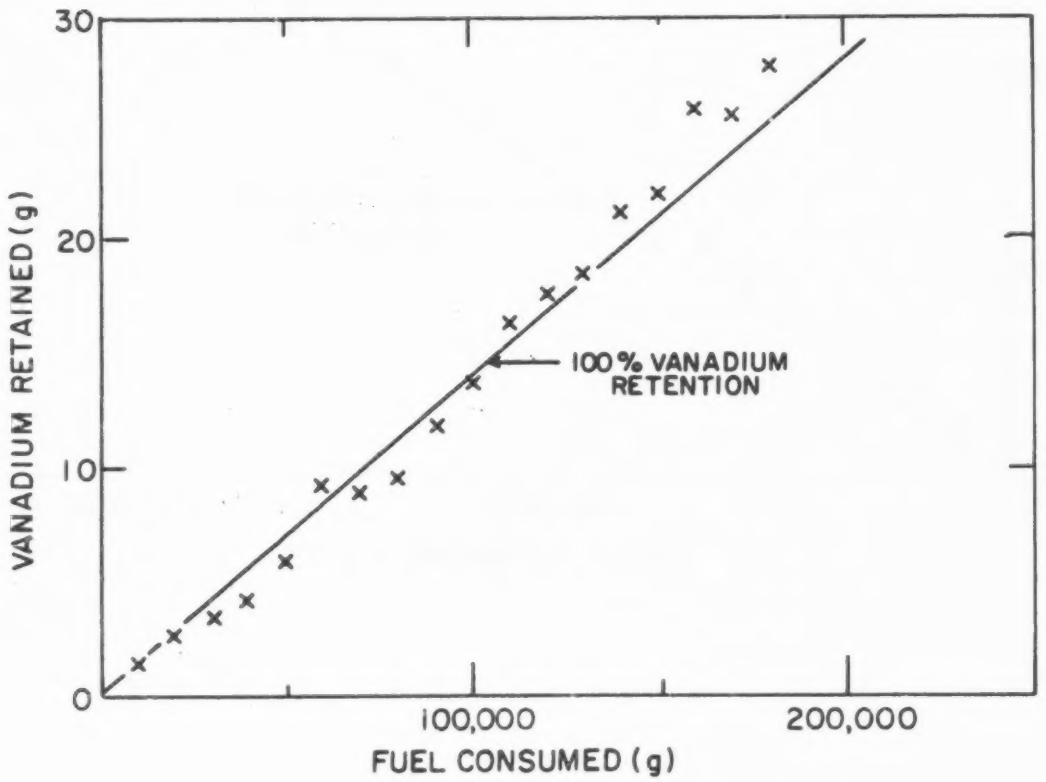


FIGURE 28

In all three cases the observed vanadium pick-up accounts for all of the vanadium fed. The iron content of the fuel oil was only 1 ppm. Thus, most of the iron in the lime must have come from iron components of the reactor such as thermocouples. The actual iron accumulated by the lime was much less than the vanadium in all three cases. These results contrast with some earlier tests (low velocity with underfiring) in which less than complete vanadium retention was observed. In those tests, the vanadium retention correlated with iron pick-up, and it appeared that the quantity of vanadium retained was only $\frac{1}{4}$ the quantity of iron picked up. Such a relationship is not evident in our current work. Major differences between conditions of the present and earlier work are higher air velocities, lower air/fuel ratios, absence of underfiring, and a fuel oil with higher vanadium content in the current work. If or how these changes are responsible for the improved vanadium recovery is not yet understood.

The CAFB lime bed has consistently picked-up about 20% of the sodium present in the fuel oil. This behaviour has continued in the present work.

(4) Gasifier Product Composition

Samples of uncombusted gasifier product have periodically been collected and analysed by gas chromatography. Analyses of three such samples are reported in Appendix C. Since heavy components condense in the sample receivers the analysis is incomplete. However, combination of the dry gas analysis with knowledge of operating conditions permits reconstruction of the quantity of carbon in the heavier components as well as the fractions of carbon and hydrogen oxidised. These results are listed below:-

Run No.	% of Carbon in C4 +	Carbon Oxidised, %	CO/CO_2 Ratio	H_2 Oxidised %
53	26.2	40.7	1.03	10
65	10.4	44.3	1.06	2.4
86	17.1	40.1	0.76	10.7

The significance of the differences observed between runs has not yet been established. However, these data do support the theory that most of the oxygen supplied is consumed in burning carbon from the lime rather than by direct reaction with the oil.

(5) Sulphur in Regenerated Lime

When fuel flow is terminated at the end of a gasification cycle, the oxygen in the fluidising air first reacts with carbon on the stone to liberate CO_2. As temperature rises and CO_2 concentration falls, a period usually exists where there

are insufficient oxides of carbon or sulphur in the off gas to account for all of the oxygen being fed. During this period the predominant reaction must be:-

$$CaS + 2O_2 \longrightarrow CaSO_4$$

When the temperature becomes high enough, SO_2 is liberated by the reactions:-

$$CaS + 1\tfrac{1}{2}\, O_2 \longrightarrow CaO + SO_2$$

$$CaS + 3Ca\,SO_4 \longrightarrow 4CaO + 4\,SO_2$$

The data indicate that the CaS is used up before the CaSO4 can be completely decomposed by the third reaction. The data in Figure 29 show that sulphur content of the regenerated stone increased rapidly during the first few cycles and then tended to line out at 2 to 2.5% on lime. The sulphur in regenerated stone was all present as sulphate. Although the individual points tended to scatter, the lined-out sulphur levels increased in the order of increasing CaO content of the different stones.

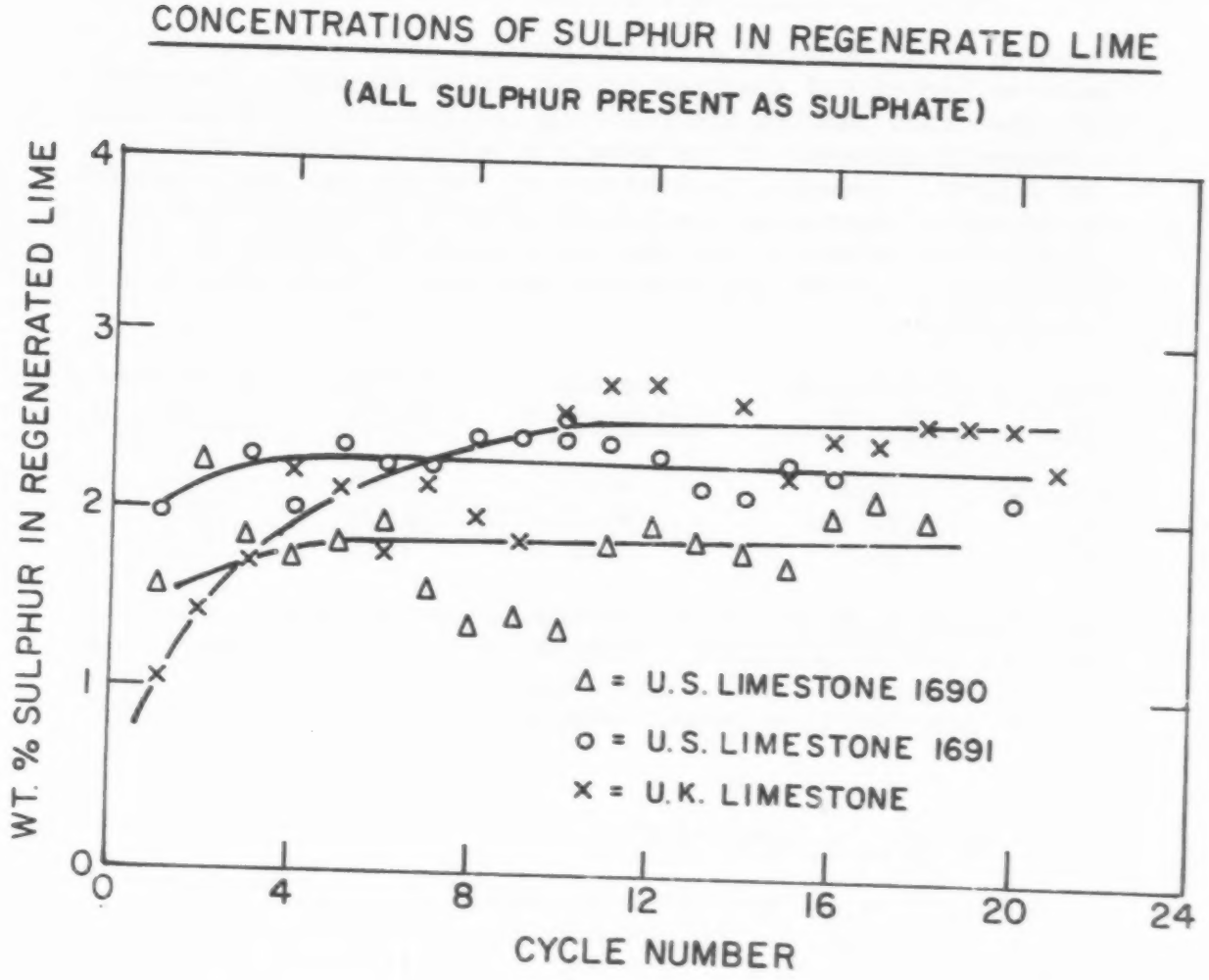


FIG. 29.

The sulphur level on the regenerated lime in these studies is slightly higher than observed in earlier tests with low velocity, underfiring, and higher air/fuel ratios. It is possible that the carbon level on the stone at the beginning of the regeneration cycle affects the sulphate level, and that carbon level was lower in the current test than was obtained with underfiring. When carbon is present, the lime is heated partly by carbon oxidation. When the lime is carbon free, all the heat to raise the temperature to regeneration conditions is supplied by the sulphate forming reaction and therefore more sulphate is formed. In a continuous regenerator, the temperature of entering lime should rise quickly to regeneration temperature and minimize the quantity of sulphate formed.

The higher sulphate levels observed in these tests do not seem to have affected sulphur removal efficiency under conditions used, as the lined-out efficiencies agree well with the results obtained under underfiring conditions.

2. Engineering Support Studies

To support design of the continuous gasifier unit, studies have been conducted of lime fluidisation velocity, solids transfer rates in the cold model of the continuous unit, and of various burner designs for combustion of the CAFB gasifier product. Since these studies have been in support of the Esso gasifier, they have been financed by Esso, but are reported here as they are pertinent to the overall CAFB project.

(a) Lime Fluidisation Velocity

A sample of limestone was calcined in the 7-inch diameter tall unit, cooled, and used for measurement of minimum fluidisation velocity. Pressure drop through the bed was measured as air rate was gradually increased. When the bed was fully fluidised, the pressure drop became constant. Figure 30 shows the curve obtained. The pressure drop reached a peak at 0.9 ft/sec and dropped to its stable level at 1.0 ft/sec. The minimum fluidisation velocity is thus 0.9 ft/sec.

A similar measurement of minimum fluidisation velocity was made for the brick dust used in the cold model of the gasifier to simulate hot lime. These data which are also shown in Figure 30, indicate a minimum fluidisation velocity of 1.3 ft/sec for the brick dust.

The new batch units just completed contain additional pressure tappings which will permit easier observation of bed density, level, and fluidisation performance. Additional studies will be made on fluidisation characteristics of lime and limestone of different particle size ranges.

FLUIDIZATION CURVES FOR LIME AND BRICK DUST

COLD AIR, 300-1200 MICRON SIZE

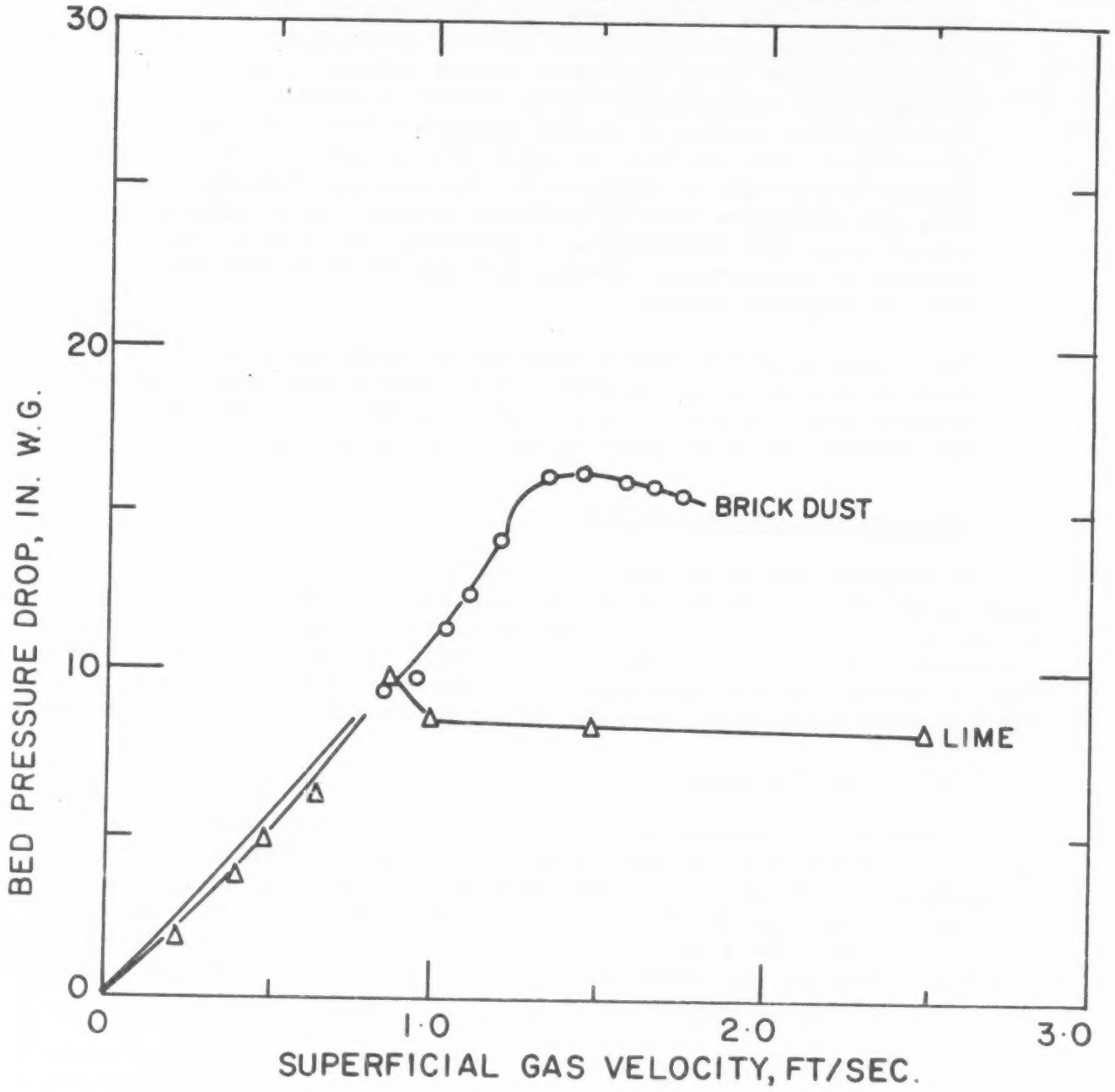


FIG. 30.

(b) Solids Transfer Rates

Tests were made to determine effects of parameters of the solids transfer system on transfer rate and air consumption. Results showing the effect of pulse frequency at different pulse rates are presented in Figure 31.

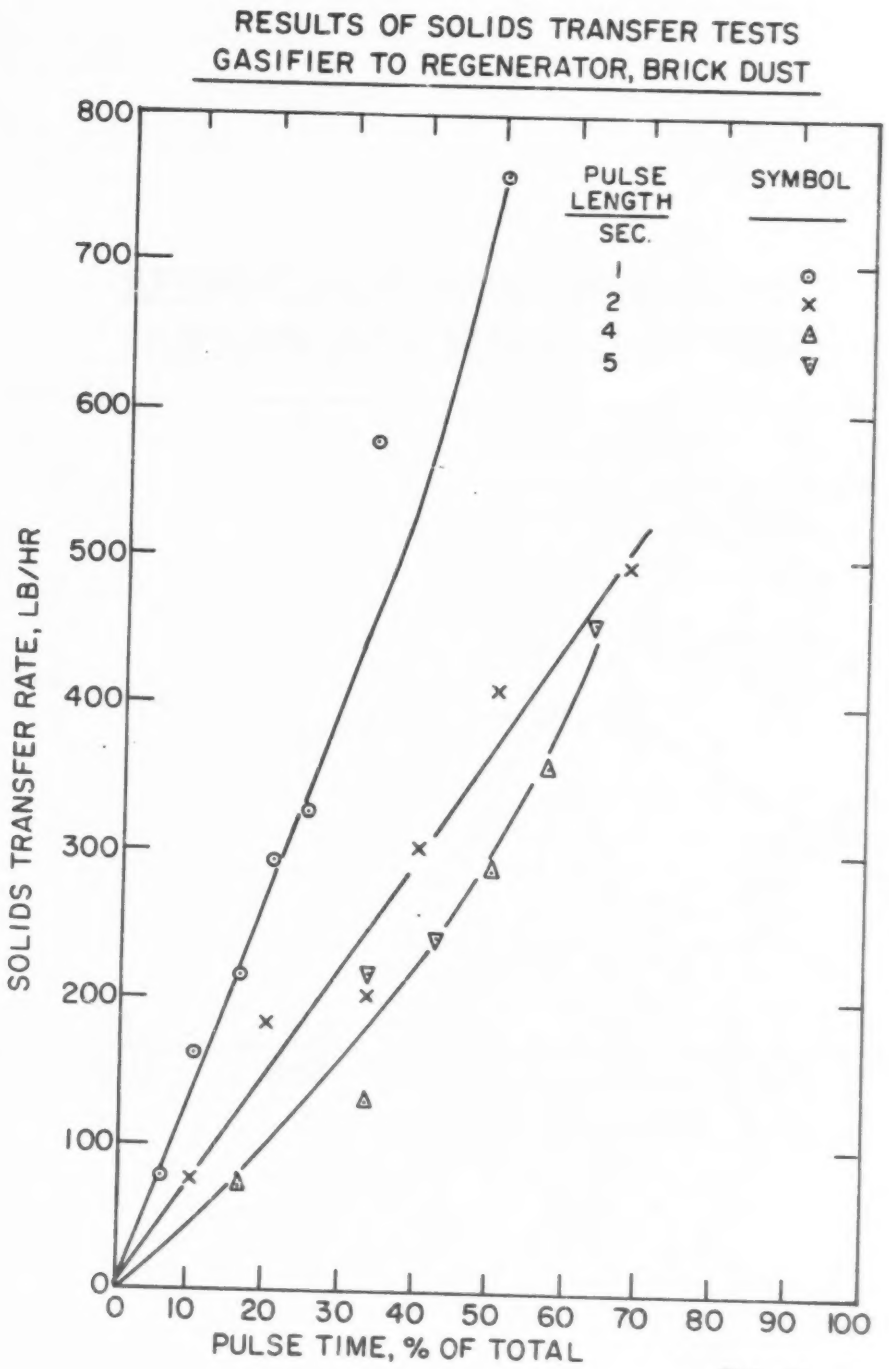


FIG. 31

These transfer rates relate to the flow from the gasifier bed to the regenerator bed. Material was drained from the bottom of the regenerator bed during the course of these tests at rates which held the bed depth constant. The drained material was weighed at the completion of each test run. It can be seen that the highest transfer rates and most efficient utilisation of the carrier gas were obtained when activating pulses of short duration were used.

Maximum rates of over 700 pounds/hour were obtained which are judged to be adequate for the continuous gasifier unit.

The efficiency of air utilisation increased with solids rate up to a level of about 300 pounds/hour. Above this rate, the pounds of solids moved per cubic foot of air remained nearly constant at about 2. This behaviour is shown in Figure 32.

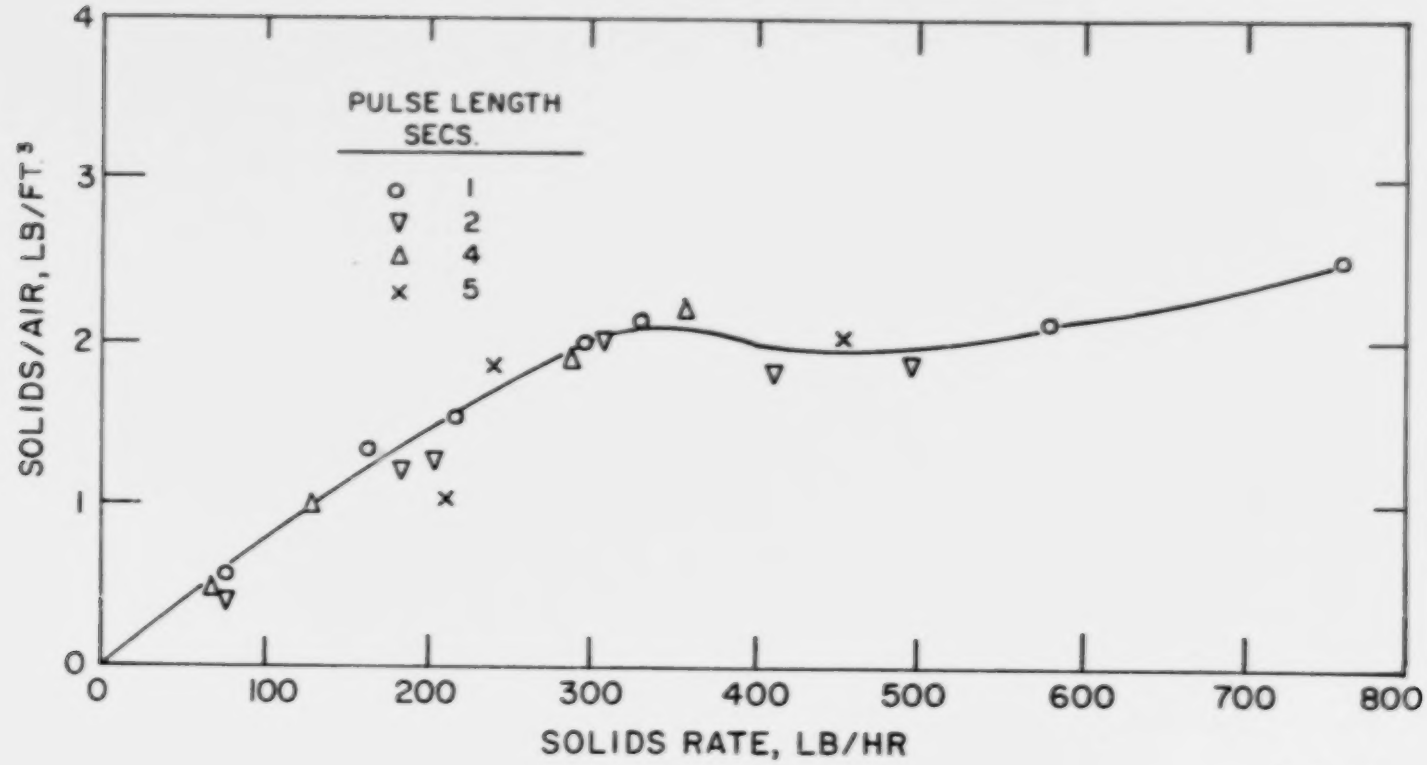


FIG. 32.

(c) Burner Design

Burners for the CAFB gasifier product will differ from normal gas burners because of the relatively large gas to air volume they will handle and because of the high temperature of the gas. Several experimental burners have been tested on the batch units as prototypes for the burner to be used with the continuous gasifier. There is no difficulty in obtaining a stable, luminous flame with the gasifier product over a range of gasifier air/fuel ratios from under 20 to over 40% of stoichiometric. The initial design, however, which brought total combustion air in through an annulus around the gas inlet, with a tangential swirl, failed to achieve sufficient air-fuel mixing to eliminate smoke. Two other designs have been tested which provide a high degree of air-fuel mixing and which give an intense, smoke-free flame. Studies of burner design are still in progress to determine the best of the designs available and to provide guidelines for estimation of commercial burner parameters.

3. Programme for Batch Unit Variable Study

An intensive study of batch unit variables with the US fuel and US limestone BCR 1691 is now getting underway in the two new batch units.

The six variables considered to be of major importance are:-

Air/fuel ratio
Temperature
Gas velocity
Bed replacement rate
Bed depth
Solids particle size

The question of whether or not underfiring was needed had been considered in the original Technical Proposal(2). However, since our results now show that underfiring is not required it will no longer be tested.

Since we wish to relate the observed effects of the variables to continuous operation, the study should ideally be based on asborption/regeneration cycles, and this was suggested in the Technical Proposal(2).

However, cyclic tests are very time-consuming, and a reasonable coverage of the variables in this manner would be prohibitive in time and cost. As a result of the poor coverage of variables offered by the original programme, a different approach is now planned which will provide more information from the same length of programme. This will be achieved by dividing the study into two parts. First of all, the variables, excluding bed make-up rate, will be examined by the fresh bed technique which will yield a great deal of information on the basic effect of each variable and also on any interactions which may occur between variables. It should also give sufficient information to allow the number of variables which need to be examined by cycles in the second part of the study to be reduced. Examination of the variables with fresh beds has the advantage that the tests are much shorter, six fresh bed tests being equivalent to one test of absorption/regeneration cycles, and good coverage of the variables should be achieved in the relatively short time of 16 unit weeks.

The programme of tests to be carried out is given in Table V. This programme will be continually reviewed as the tests proceed. It is based on a sequential examination of the variables. The design is such that not only will we get detailed information on the basic effect of each variable, but we will also get an indication of interactions which exist between variables. Any interactions which become evident will be examined further. It is worth noting that a full factorial design has been considered but was rejected because our existing information on the behaviour of the variables is not sufficient to guarantee that the results from such a design would be meaningful. When, as in our case, it is possible to obtain results from individual runs before the entire experimental programme is completed, sequential experiment designs are much more efficient than factorial type designs.

TABLE V

Fresh Bed Test Programme

Test	% Stoich Air	Temp °C	Gas Vel. ft./sec.	Reagent Particle Size (microns)	Static Bed Depth (ins.)
1	30	870	6	300 - 3000	15.5
2	25	870	6	"	15.5
3	20	870	6	"	15.5
4	15	870	6	"	15.5
5	25	800	6	"	15.5
6	25	950	6	"	15.5
7	25	1000	6	"	15.5
8	20	800	6	"	15.5
9	20	950	6	"	15.5
10	25	870	4	"	15.5
11	25	870	8	"	15.5
12	20	870	4	"	15.5
13	20	870	8	"	15.5
14	25	870	6	600 - 1400	15.5
15	25	870	6	1200 - 3000	15.5
16	20	870	6	600 - 1400	15.5
17	20	870	6	1200 - 3000	15.5
18	25	870	6	300 - 3000	10
19	25	870	6	"	20
20	20	870	6	"	10
21	20	870	6	"	20
22	25	1000	4	"	15.5
23	25	1000	8	"	15.5
24	25	1000	6	600 - 1400	15.5
25	25	1000	6	1200 - 3000	15.5
26	25	1000	6	600 - 1400	10
27	25	1000	6	300 - 3000	20
28	25	870	8	600 - 1400	15.5
29	25	870	8	1200 - 3000	15.5
30	25	870	8	300 - 3000	10
31	25	870	8	300 - 3000	20
32	25	870	6	1200 - 3000	10
33	25	870	6	1200 - 3000	20

(a) Range of Variables for Fresh Bed Tests

The fuel oil to be used in the intensive variable study was obtained from Creole Petroleum Co. It is a Venezuelan heavy fuel oil with the following properties:-

Gravity	16.5 API
Flash Point	154 F
Sulphur	2.14%
Viscosity	178 SSF at 122 F

The limestone is BCR 1691 obtained from Warren Brothers Road Co., Seneca Falls, New York. The stone will be crushed and sieved to the required particle size range at Esso Research Centre.

Previous studies have indicated the general region of conditions for reasonable CAFB operation. Therefore, the new variable study will be concentrated in a fairly narrow range.

The current experimental plan differs in three respects from the version proposed in our second monthly report[4]; 20% of stoichiometric will replace 15% as the lower comparison level of air fuel ratio, and a wide range particle size of lime will replace the narrow cut for the baseline level of this variable, and 6 ft/sec. will be the baseline air velocity.

A higher air/fuel ratio has been selected because the recent data have indicated that 15% of stoichiometric is probably near or below the limit of operability under some conditions.

The wide range lime particle size will be investigated to determine feasibility of using lower cost stone. Discussions with limestone producers have indicated that the lowest cost size range of stone available is the $\frac{1}{8}$-down fraction which is nearly a waste product in many operations. Screen analyses on different lots of $\frac{1}{8}$-down Denbighshire stone indicate that the 600-1200 micron fraction was only 15 to 20% of the total. There is considerable incentive to use as wide a particle size range as possible to minimise total lime requirements and to avoid grinding and screening. Several preliminary tests are therefore planned to test general operability with different size ranges before deciding on the exact ranges to be included in the detailed variable study. If operability permits we will include a very wide fraction such as the $\frac{1}{8}$ down (3000 micron) as well as narrower cuts of small and large fractions. Present intentions are to use 600-1400, 300-3000 and 1200-3000 micron fractions.

(b) Cyclic Tests

Although fresh bed tests can provide a measure of initial sulphur removal efficiency under a variety of conditions, they cannot measure bed activity maintenance under cyclic conditions, and they cannot measure the effects of lime replacement rate. Cyclic tests will be used to study these variables under conditions to be selected from results of the fresh bed tests. Thirteen tests of 20 cycles each are planned.

D. Conclusions and Recommendations

The CAFB studies in this report period have led to the following conclusions and recommendations.

1. Conclusions

(a) Air fuel ratios of 25% of stoichiometric are required to maintain high sulphur removal efficiencies (95%) up to 10% or more calcium oxide utilisation. The conditions which permit occasional high sulphur removal runs at air/fuel ratios as low as 21% of stoichiometric are not understood. Usually the efficiency falls off as air/fuel ratio is lowered from the 25% of stoichiometric level.

(b) A high pressure drop distributor design ($\frac{1}{8}$-inch holes) gives more reproducible and slightly higher levels of sulphur removal efficiency than the low pressure drop design (3/16-inch holes) used in the past. This conclusion differs from that drawn in Monthly Report No.7[9] but is based on evaluation of the complete range of data rather than just the January data.

(c) Poor sulphur removal efficiency correlates with high levels of carbon on the lime. Carbon on lime becomes insignificant at about the same air/fuel ratio (25% of stoichiometric) at which sulphur removal efficiency approaches 100%.

(d) The US fuel oil originally selected by APCO performs well under CAFB gasification conditions and is suitable for an intensive variable study.

(e) US limestone BCR 1691 performs well under CAFB conditions. It has only 81% of the CaO content of the UK stone used as a standard, but at an equal CaO replacement rate it gives the same lined out sulphur removal efficiency.

(f) US limestone BCR 1690 is inferior to the UK standard and to 1691. It contains only 60% as much CaO as 1691, it suffers greater attrition, it gives lower sulphur removal efficiency even when replaced at equal CaO/S rates, and it tends to sinter and agglomerate under CAFB cyclic conditions. It is therefore not suitable for this programme.

(g) Complete vanadium removal from the fuel can be attained under CAFB gasifying conditions with the UK stone and with both US limestones tested, even under conditions giving less iron than vanadium accumulation on the lime. The CAFB removes only 20% of the fuel sodium.

(h) Most of the oxygen supplied to the CAFB gasifier is used to oxidise carbon. At 24% stoichiometric air, about 40% of the fuel carbon is oxidised compared with 10% or less of the hydrogen.

(i) Sulphur contents of 2 to 3% (as sulphate) on regenerated stone are encountered at 24% of stoichiometric air in the absence of underfiring, but activity of the lime for sulphur pick-up is not reduced below levels obtained with only 1-2% sulphur on regenerated stone.

(j) Minimum fluidisation velocity of 800-1200 micron lime used in batch unit studies is 0.9 ft/sec.

(k) Solids transfer rates of 700 lb/hr. can be obtained with the transfer system designed for the continuous gasifier pilot plant. About two pounds of solids per cubic foot of air are transferred at rates over 300 pounds/hour.

2. Recommendations

(a) Twenty percent of stoichiometric should be used as the lower base level of air fuel ratio for the batch units CAFB variable study with US fuel and lime.

(b) The high pressure drop distributor should be used in the batch units for the intensive variable study.

(c) Development of an analytical procedure for carbon on lime should be continued to provide a measure of the rate and level of carbon accumulation during the batch gasification cycle.

(d) The US fuel oil originally selected by APCO, a Venezuelan heavy fuel oil of about 2.2% sulphur, should be used for the intensive CAFB variable study.

(e) US limestone BCR 1691 from Warren Brothers Road Co., Seneca Falls, New York, should be used for the intensive variable study.

(f) No further CAFB work is recommended on US limestone BCR 1690.

III REFERENCES

(1) Moss, G.: The Desulphurising Combustion of Fuel Oil in Fluidised Beds of Lime Particles, Handout at First International Conference on Fluid Bed Combustion, at Hueston Woods, Onio, November 1968.

(2) Technical Proposal for Study of Chemically Active Fluid Bed Technique for Reduction of Sulphur Oxides Emissions. Report ER-13M-69 by Esso Research Centre, Abingdon, Berkshire, July 11th 1969.

(3) Craig, J.W.T., Johnes, G.L. and Moss, G.: Study of Chemically Active Fluid Bed Gasifier for Reduction of Sulphur Oxide Emissions, Monthly Progress Report No. 1, APCO Contract CPA 70-46, Esso Research Centre, Abingdon, Berkshire, July 1970.

(4) Craig, J.W.T., Johnes, G.L., Moss, G., Taylor, J.H.: Study of Chemically Active Fluid Bed Gasifier for Reduction of Sulphur Oxide Emissions, Monthly Progress Report No. 2, APCO Contract CPA 70-46, Esso Research Centre, Abingdon, Berkshire, August 1970.

(5) Ibid - Report No. 3, September 1970

(6) Ibid - Report No. 4, October 1970

(7) Ibid - Report No. 5, November 1970

(8) Ibid - Report No. 6, December 1970

(9) Ibid - Report No. 7, January 1971

APPENDIX A

RESULTS OF WORK JUST PRIOR TO CONTRACT

This appendix summarises results obtained by the Esso Research Centre on the CAFB gasifier in the period between submission of the Technical Proposal(2) to APCO and signing of the contract. These studies were carried out with the UK fuel and Denbighshire limestone whose properties are listed in Tables B-I and B-II of Appendix B.

A. Reagent Life

The effect of successive absorption/regeneration cycles on reagent activity during partial combustion has been studied at different bed make-up rates and mean particle size. Absorption was carried out at a stoichiometric air rate between 30 and 35%, a superficial gas velocity of 2.5 ft/sec. and a bed temperature between 800 and 900°C. In each absorption period the bed was exposed for a total of 100 minutes, during which its sulphur content rose to between 3 and 4%. Regeneration was carried out by shutting off the fuel supply and allowing air alone to contact the bed. Bed samples were taken for sulphur analysis at the beginning and end of each absorption period, and a regular check was made on bed losses; fresh material being added to the bed after each cycle to make up for attrition and sampling losses. Bed make-up rate was controlled by adjusting the number and size of the samples. Varying mean particle size in a downward direction only was considered since an increase would be unlikely to give a beneficial effect. This was achieved in the low gas velocity batch fluidiser by fitting baffles above the bed which gave better retention of the smaller particles and also by changing the size distribution of the limestone feed to 600-1200 μ from the original 850-1200 μ. These alterations gave a reduction in mean particle size of lime in the bed from 810 to 635 μ.

Figure A-1 illustrates the effect that successive absorption/regeneration cycles can have on reagent activity.

These results show that, under the particular operating conditions employed, the desulphurising efficiency dropped from 100% to a fairly steady level of 60% and that this steady level was reached in less than 10 cycles. The rapid drop in efficiency is typical of all tests where a steady level of less than 100% was observed.

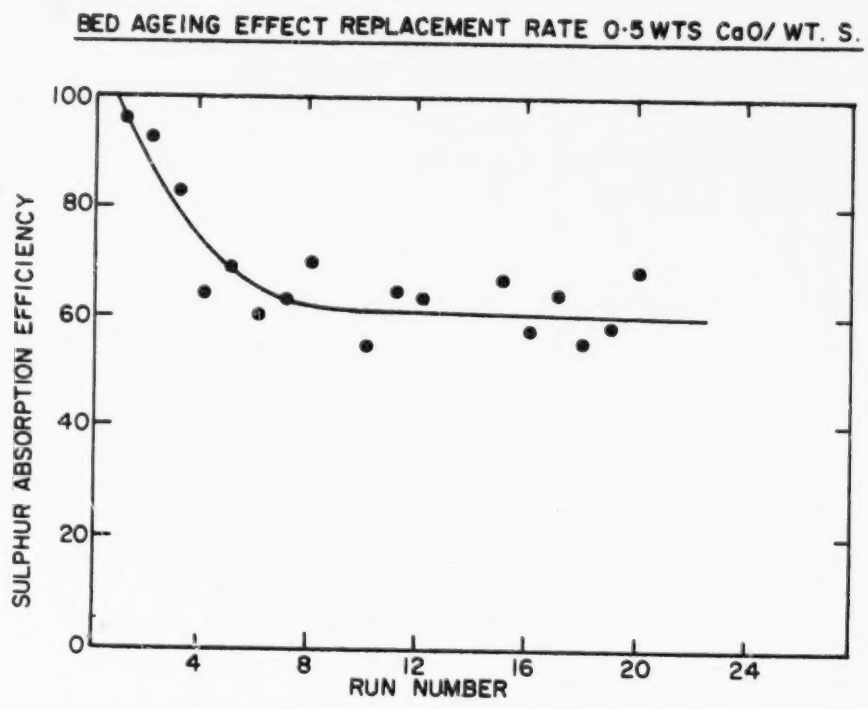


FIGURE A-1

Figure A-2 summarises the results obtained in tests on the effect of bed make-up rate and mean particle size.

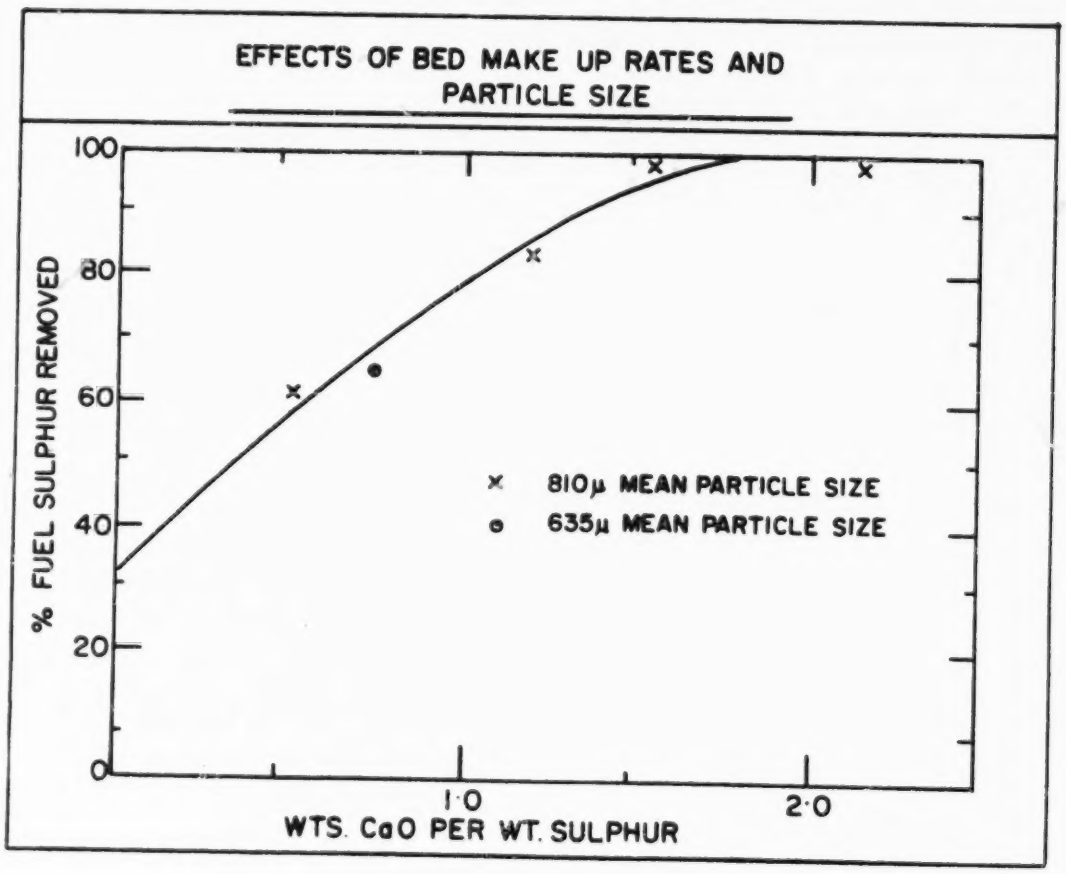


FIGURE A-2

These show that at bed make-up rates in excess of 1.8 wts. CaO per wt. of sulphur, a desulphurising efficiency of 100% can be maintained indefinitely and that at lower make-up rates, the efficiency falls off rapidly. At 1.8 wts CaO per wt of sulphur, the reagent cost is estimated at 5c/bbl of a 3% sulphur fuel. Reducing the mean particle size has no significant effect on the steady level of desulphurising efficiency within the limited range covered.

B. Retention of Sodium and Vanadium by the Bed

During the life tests, the retention by the bed of sodium and vanadium present in the fuel oil was studied.

Sodium pick-up was found to be consistently low, being less than 20% of the amount introduced.

The results obtained on vanadium retention were more encouraging but also more diverse. Under conditions of partial combustion, the efficiency of vanadium pick-up varied from test to test between the levels of 35% and 100% and was not related to bed make-up rate (Figure A-3).

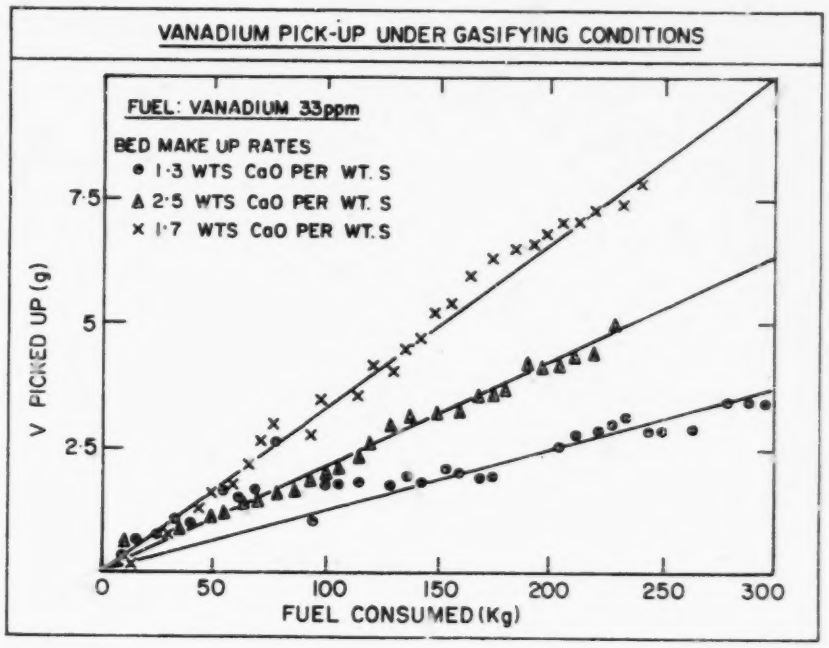


FIGURE A-3

A correlation was found to exist however between rate of vanadium pick-up and rate of iron pick-up (Figure A-4). The iron originated from the metal components of the unit which protrude into the bed.

It would appear then that the fuel vanadium can be retained in the bed by introducing iron into the bed at a rate five times greater than the rate vanadium is being introduced.

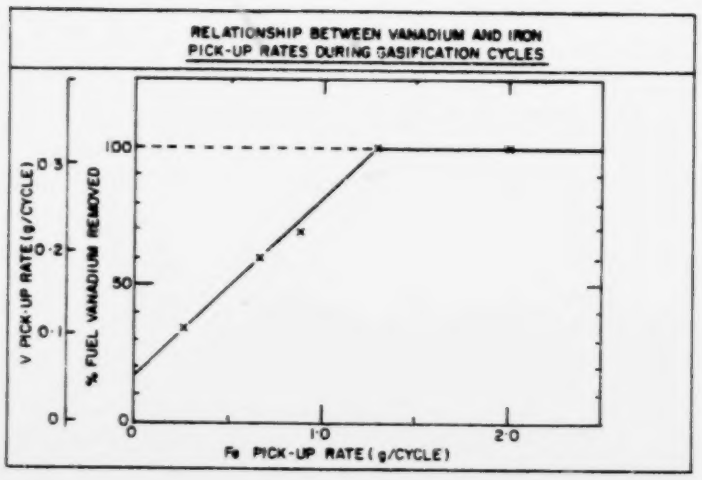


FIGURE A-4

C. Gasification without Underfiring

All gasification tests previously reported have been carried out in the low gas velocity batch fluidiser at supercicial gas velocities of less than 3 ft/sec. At these velocities, the combustion of kerosine below the distributor was necessary to preheat the fluidising air and so prevent the deposition of coke at and below the level of the fuel injectors. The utilisation of 25% of the incoming air in this way has resulted in the sulphur being evenly distributed throughout the bed as calcium sulphide. Tests carried out early in 1970 in a new gasifier have, however, shown that underfiring is unnecessary when superficial gas velocities in excess of 3 ft/sec are employed. Operating without underfiring almost certainly prolongs distributor life and, for this reason alone, it is the preferred mode of operation. However, it also makes the bed more complex chemically in that there is a transition from calcium sulphate to calcium sulphide with increasing distance from the distributor and, along with this, an increase in total sulphur content. These effects result from the additional oxygen entering through the distributor. This oxygen reacts with the clacium sulphide below the level of the fuel injectors and at the temperature of the absorbing bed (800-900° C) predominantly forms calcium sulphate. The sulphur dioxide which is released during the less favourable formation of calcium oxide is reabsorbed as calcium sulphide above the level of the fuel injectors.

The effect of this change in operation on the variables affecting desulphurising efficiency has been studied to some extent. Results so far show that an operating temperature between 800 and 900° C is still to be preferred. However, the influence of stoichiometric air rate has changed radically as is evident in Figure A-5 where the effects of stoichiometric air rate on the desulphurising efficiency of fresh beds are compared with and without underfiring.

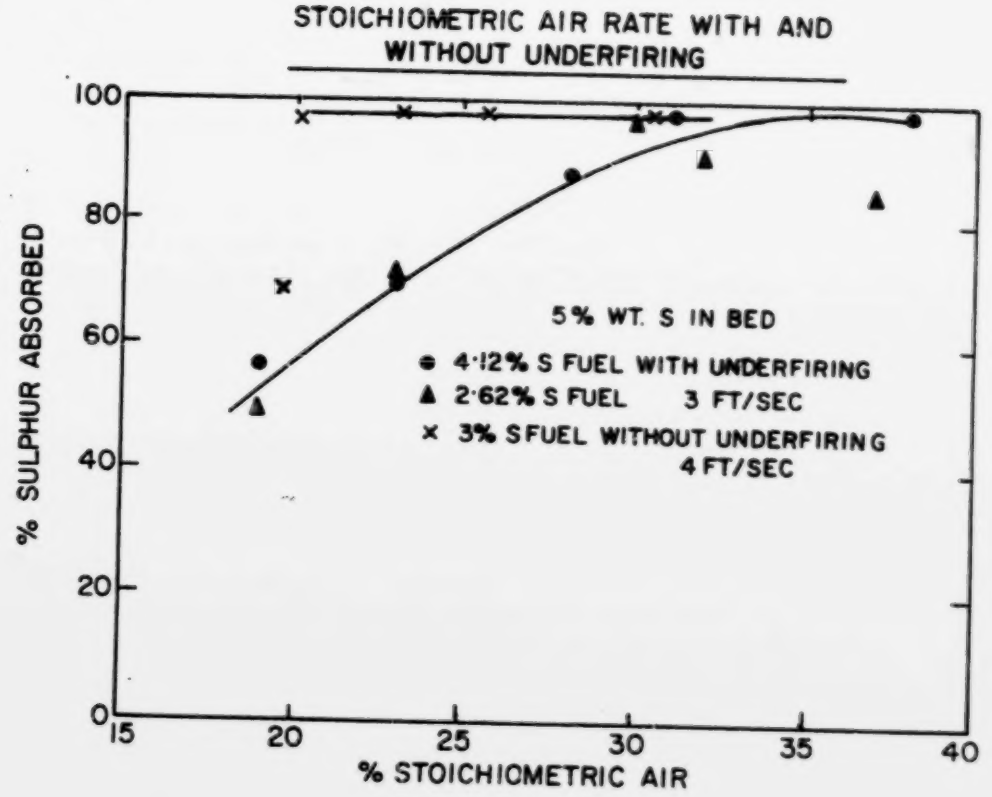


FIGURE A-5

Figure A-6 shows the manner in which desulphurising efficiency varied with increasing CaO utilisation during the course of these high velocity runs. Except for the run at 20.7% of stoichiometric air, the lime maintained its activity to over 20% of utilisation.

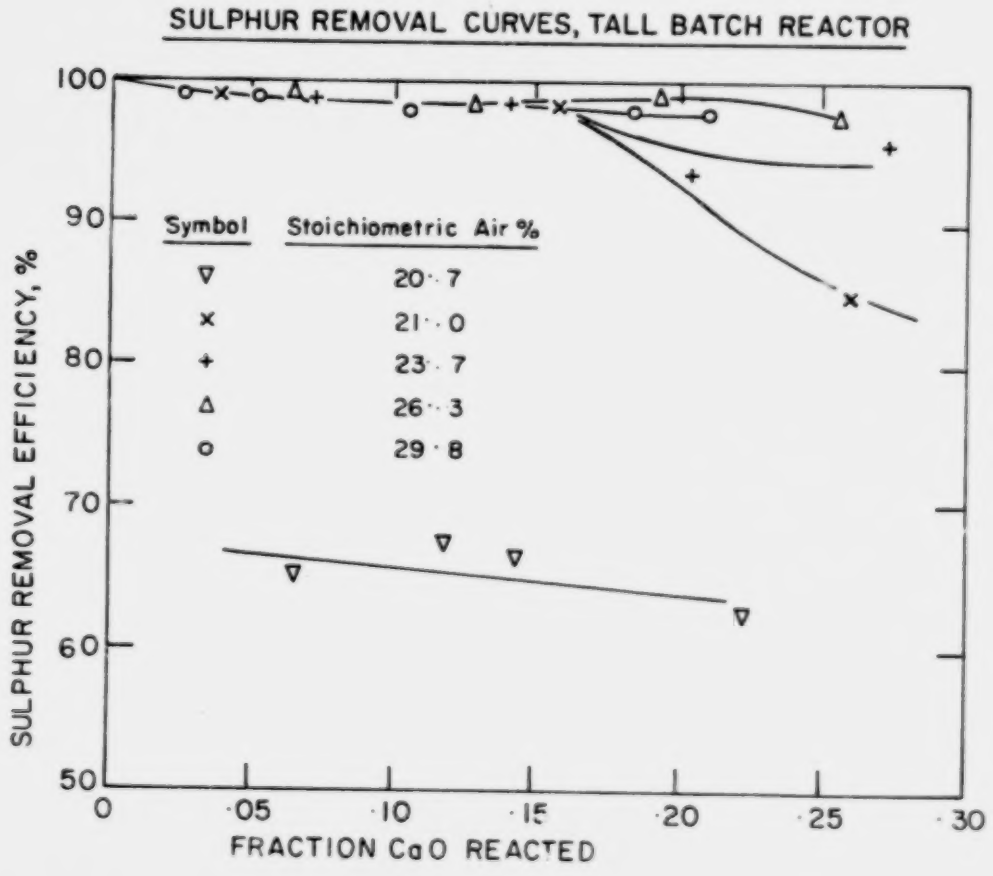


FIG A 6.

It is evident that with no underfiring high desulphurising efficiency can be maintained at lower stoichiometric air rates. If it is assumed that the drop in efficiency previously observed with reductions in stoichiometric air rate was due to the observed build-up of carbon on the particles, then it is likely that the current improvement is due to an increased amount of carbon being removed from the bed in the oxidising zone resulting in a continual supply of carbon-free stone to the gasifying region.

To be able to operate at the lower stoichiometric air rate and higher gas velocity is a great advantage since it means that the fuel throughput is doubled for a fluid bed of given cross-sectional area.

Multicycle tests reveal no significant effect of the absence of underfiring on the relationship between lime replacement rate and the lined-out efficiency of sulphur removal. The line established in the absence of underfiring, Figure A-7, is quite similar to that found with underfiring, Figure A-2. The data in Figure A-7 were obtained at 25% of stoichiometric air compared with 30-35% used with the underfiring tests in Figure A-2.

EFFECT OF MAKE-UP RATE ON DESULPHURISING EFFICIENCY

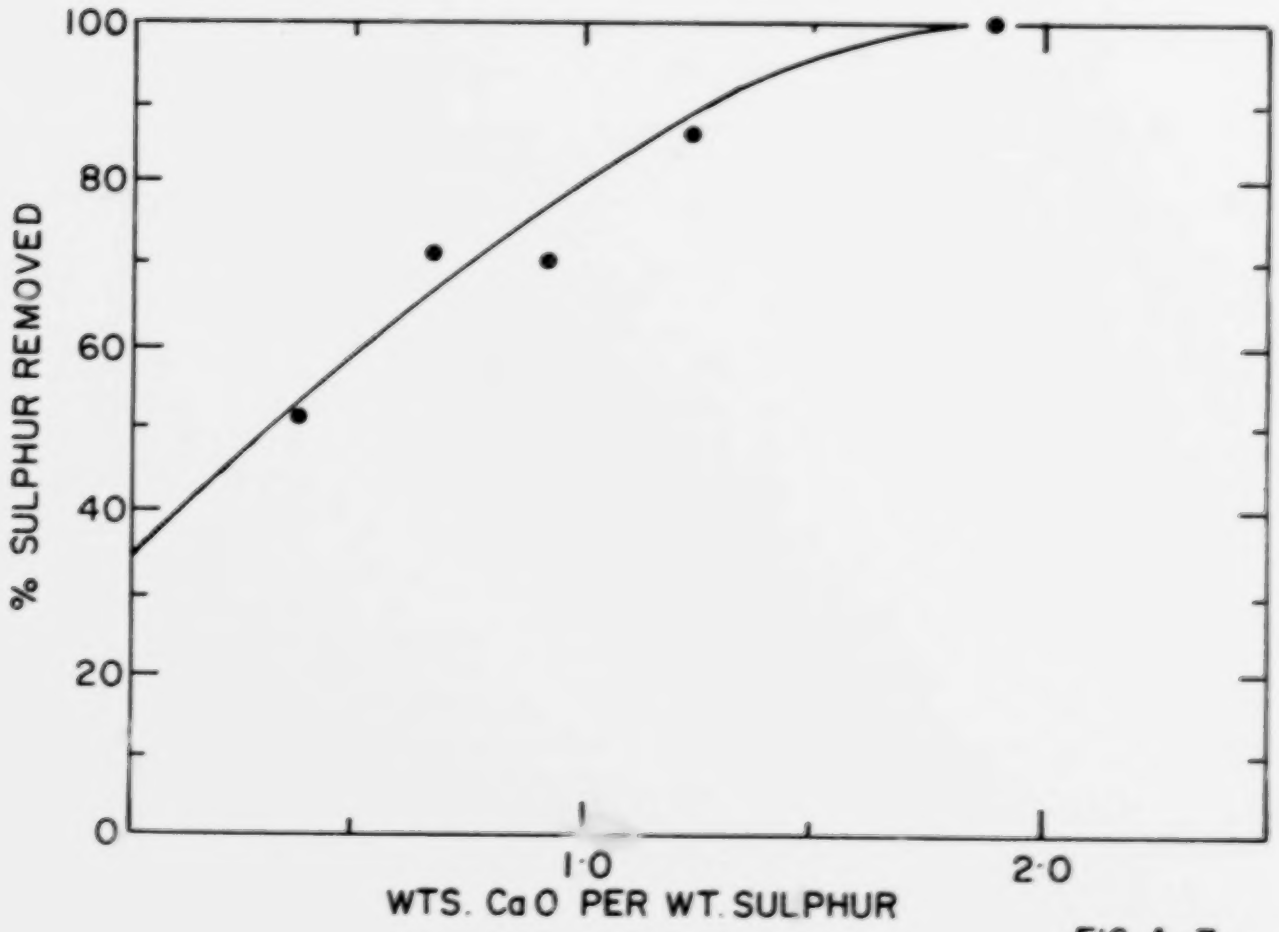


FIG. A.-7

APPENDIX B

FUEL AND LIME ANALYSES

TABLE B-1

ANALYSIS OF TEST FUEL OILS

Property		UK Test Fuel	US Test Fuel
Specific Gravity		0.95	0.95
Kinematic viscosity (cs)	at 140 F	98.2	-
	at 180 F	-	54.7
	at 210 F	26.2	-
Carbon	% by wt	84.8	85.9
Hydrogen	% by wt	11.6	11.5
Sulphur	% by wt	3.03	2.22
Vanadium	ppm	140	270
Nickel	ppm	20	-
Sodium	ppm	37	13
Iron	ppm	1	4
Asphaltenes	% by wt	3.72	6.3
Conradson Carbon	% by wt	9.32	7.5

TABLE B-2

ANALYSIS OF TEST LIMESTONES

Component	Content. % by wt.		
	UK	United States	
	Denbighshire	1691	1690
CaO	55.2	45.0	26.7
MgO	0.27	2.02	17.5
SiO_2	0.32	14.2	13.5
Fe_2O_3	0.07	0.53	0.83
Al_2O_3	0.06	1.14	5.10
Na_2O	0.03	0.17	0.19
CO_2 released	43.4	35.4	35.5
S as SO_3	-	1.0	0.59

APPENDIX C

CAFB BATCH REACTOR DATA - 1-A UNIT RESULTS

TABLE C-1

CAFB BATCH UNIT TEST CONDITIONS

Run No.	Fuel	Limestone	Limestone Particle Size μ	Fuel Rate (g/min)	Air Rate (L/min)	Superficial air vel. (ft/sec.)	% Stoich. Air	Temperature C	
								Initial	Average
11(c)	UK(a)	UK	800 - 1200	200	473	4.3	21.7	770	865
22(c)	"	"	"	150	441	4.0	27.0	790	840
23(c)	US(b)	"	"	150	435	3.9	26.6	790	830
25(c)	UK(a)	"	"	200	440	3.9	20.2	780	835
26	"	"	"	195	450	4.1	21.0	830	840
27	"	"	"	200	443	4.0	20.3	850	840
28A	"	"(d)	"	200	464	4.2	21.3	840	840
28B	"	"(d)	"	200(e)	459	4.2	21.1	860	850
28C	"	"(d)	"	200(f)	420	3.8	19.3	790	840
29	"	"(d)	"	200	480	4.4	22.0	915	860
30	"	"(d)	"	200	471	4.3	21.6	730	870
32	"	UK(d)	"	200	434	4.0	19.9	900	840

(a) U.K. fuel 3.03% S
(b) U.S. fuel 2.22% S
(c) Fuel injected to bed centre
(d) Used bed of lime employed in test
(e) 1.5 CFM air to fuel nozzle
(f) 0.5 CFM air to fuel nozzle (other tests use 1.0 CFM air to fuel nozzle)

TABLE C-1

CAFB BATCH UNIT TEST CONDITIONS

(Cycle Test, UK Fuel and Limestone)

Run No.	Cycle	Air Rate l/min.	Superficial Gas Vel. ft/sec	Fuel Rate g/min	% Stoich Air	Feed Particle Size μ	Bed Depth (Static) in.	Limestone Make-up Rate g/cycle	Average Bed Temp. (Absorption) °C	Max. Bed Temp. (Regeneration) °C
33	1	426	3.9	165	23.7	850-1400	15.5	400	860	1050
34	2	432	3.9	"	24.0	"	-	"	880	1060
35	3	439	4.0	"	24.4	"	-	"	870	1080
36	4	448	4.1	"	24.9	"	15.4	"	870	1070
37	5	444	4.1	"	24.7	"	-	"	880	1080
38	6	442	4.0	"	24.6	"	15.6	"	890	1070
39	7	442	4.0	"	24.6	"	-	"	890	1080
40	8	423	3.9	"	23.5	"	15.2	"	880	1070
41	9	424	3.9	"	23.6	"	-	"	900	-
42	10	412	3.8	"	22.9	"	-	"	880	-
43	11	423	3.9	"	23.5	"	15.7	"	880	1070
44	12	415	3.8	"	23.1	"	-	"	870	1060
45	13	438	4.0	"	24.3	"	15.2	"	880	1070
46	14	414	3.8	"	23.0	"	-	"	880	1090
47	15	414	3.8	"	23.0	"	-	"	890	1080
48	16	413	3.8	"	23.0	"	-	"	890	1070
49	17	424	3.9	"	23.6	"	15.2	"	880	1060
50	18	422	3.9	"	23.5	"	-	"	880	1080
51	19	418	3.8	"	23.2	"	-	"	880	1070
52	20	426	3.9	"	23.7	"	-	"	880	1070
53	21	419	3.8	"	23.3	"	15.2	"	880	1070

70

60 minute absorption cycle

Low pressure drop distributor

TABLE C-1

CAFB BATCH UNIT TEST CONDITIONS

(Cycle Test UK Fuel and US Limestone 1691)

Run No.	Cycle	Air Rate l/min.	Superficial Gas Vel. ft/sec	Fuel Rate g/min	% Stoich Air	Feed Particle Size μ	Bed Depth (Static) in.	Limestone make-up Rate g/cycle	Average Bed Temp. (Absorption) °C	Max. Bed Temp. (Regeneration) °C
54	1	441	3.9	165	24.5	600-1400	16.5	-	840	1050
55	2	447	4.0	165	24.8	"		500	850	1060
56	3	461	4.2	165	25.6	"		500	865	1060
57	4	411	3.8	165	22.9	"	16.0	500	880	1060
58	5	422	3.9	165	23.4	"		500	875	1070
59	6	414	3.8	165	23.0	"		500	875	1070
60	7	408	3.8	165	22.7	"		500	855	-
61	8	419	3.8	165	23.3	"	16.1	500	855	-
62	9	433	4.1	165	24.1	"		500	875	1090
63	10	415	3.8	165	23.1	"		500	885	1080
64	11	415	3.9	165	23.1	"		500	885	1080
65	12	419	3.9	165	23.3	"		500	885	1080
66	13	416	3.8	165	23.1	"		500	870	1080
67*	14	394	3.6	165	21.9	"	16.1	500	860	1070
68	15	413	3.8	165	23.0	"		500	865	1080
69	16	411	3.8	165	22.8	"		500	870	1090
70	17	407	3.7	165	22.6	"		500	865	1080
71	18	403	3.7	165	22.4	"		500	870	1070
72	19	394	3.7	165	21.9	"		500	880	1080

7/

60 minute absorption cycle

Low pressure drop distributor

* 2nd attempt at cycle. In 1st attempt fuel pump failure after 21 min and spontaneous regeneration.

TABLE C-1

CAFB BATCH UNIT TEST CONDITIONS

(Cycle Test UK Fuel and US Limestone 1690)

Run No.	Cycle	Air Rate l/min.	Superficial Gas Vel. ft/sec	Fuel Rate g/min	% Stoich Air	Feed Particle Size μ	Bed Depth (Static) in. Start Cycle	Bed Depth (Static) in End Cycle	Limestone make-up Rate g/cycle	Average Temp. (Absorption) °C	Max. Bed Temp. (Regeneration) °C
78	1	399	3.6	165	22.2	600-1400	15.5	13.4	-	845	1080
79	2	412	3.7	"	22.9	"	15.6	-	1800	850	1060
80	3	413	3.7	"	23.0	"	-	-	"	830	1060
81	4	408	3.7	"	22.7	"	-	-	"	845	1070
82	5	431	3.7	"	24.0	"	-	18.1	"	840	1070
83	6	412	3.7	"	22.9	"	16.9	-	"	855	1090
84	7	434	4.0	"	24.1	"	-	-	"	860	1080
85	8	473	4.3	"	26.3	"	-	-	"	870	1080
86	9	430	3.9	"	23.9	"	-	-	"	865	1080
87	10	441	4.1	"	24.5	"	-	16.8	"	870	1050
88	11	396	3.6	"	22.0	"	16.1	-	840	860	1060
89	12	432	4.0	"	24.0	"	-	-	"	880	1070
90	13	422	4.0	"	23.5	"	-	-	"	890	1070
91	14	422	4.0	"	23.5	"	-	-	"	890	1070
92	15	420	3.9	"	23.3	"	-	15.5	"	890	1080
93	16	385	3.5	"	21.6	"	15.9	-	"	845	1070
94	17	385	3.5	"	21.6	"	-	-	"	830	1060
95	18	400	3.7	"	22.2	"	-	14.2	"	865	1060

72

60 minute absorption cycle

Low pressure drop distributor

TABLE C-1

CAFB BATCH UNIT TEST CONDITIONS

Run No.	Fuel	Lime-Stone	Limestone particle size μ	Fuel Rate g/min	Total Air Rate l/min	Superficial Gas Vel. ft/sec.	% Stoich. Air	Bed Depth (in) (Static) Start	Bed Depth (in) (Static) End	Average Bed Temp. (Absorption) °C	Max. Bed Temp. (Regeneration) °C	Duration of Absorption (min.)
96	UK(3.05%S)	UK	600-1400	210	441	3.9	19.3	15.5	14.2	800	1090	300
98	"	"	"	208	433	3.9	19.1	"	14.4	815	1080	126
99	"	"	"	195	435	3.9	20.5	"	14.2	810	1070	120
100	"	"	"	245	540	4.8	20.2	"	13.8	810	1090	90
101	"	"	"	184	444	4.1	22.1	"	14.2	850	1090	120
102	"	"	"	175	435	4.1	22.8	"	14.6	860	1090	120
103	US(2.22%S)	US(1691	"	165	446	4.2	24.8	"	14.2	865	1090	240
104	UK(3.05%S)	UK	"	173	440	4.1	23.3	"	14.4	860	1080	120
105	"	"	"	165	433	4.0	24.1	"	14.2	845	1070	120
106	"	"	"	142	454	4.2	29.3	"	14.2	860	1050	205
107	"	"	"	206	449	3.8	20.0	"	-	740	1000	60
108A	"	"	"	206	453	3.9	20.2	-	-	770	-	30
108B	"	"	"	165	456	4.1	25.4	-	14.4	820	1010	30
109(a)	"	"	"	206	445	4.0	19.8	15.5	15.6	810	-	120

High pressure drop distributor

(a Run ended without regeneration, cooled under nitrogen blanket

TABLE C-1

CAFB BATCH UNIT TEST CONDITIONS

Run No.	Fuel	Lime-Stone	Limestone Particle Size Range μ	Fuel Rate (g/min	Total Air Rate (l/min	Superficial Gas Vel. ft/sec.	% Stoich. Air	Bed Depth (in) (Static Start	End	Average Bed Temp. (Absorption) °C	Max. Bed Temp. (Regeneration) °C	Duration of Absorption (min.)	Distributor
110	UK. 3.03%S	UK	600-1400	207	401	3.5	17.7	15.5	14.2	810	1090	129	Normal
111	"	"	"	190	430	3.8	20.7	15.5	14.0	820	1085	120	"
112	"	"	"	161	449	4.1	25.2	15.5	14.4	855	1090	124	"
113	"	"	"	163	433	3.8	24.2	15.5	14.0	825	1060	125	"
114	"	"	"	176	415	3.6	21.5	15.5	14.1	815	1065	122	"
115	"	"	"	150	419	3.8	25.6	15.5	14.4	850	1090	123	"
116	"	"	"	204	429	3.6	19.3	15.5	14.3	780	1055	122	High Pressure Drop
117	"	"	"	205	444	3.8	19.9	15.5	14.0	790	1060	120	"
118	"	"	"	190	400	3.5	19.3	15.5	14.2	815	1080	120	"
119	"	"	"	205	423	3.6	18.9	15.5	14.2	790	1070	120	"
120	"	"	"	173	420	3.7	22.3	15.5	14.4	830	1080	120	"
121	"	"	"	150	436	3.9	26.7	15.5	14.3	850	1060	120	"

TABLE C-2

SULPHUR REMOVAL IN FRESH BED BATCH REACTOR TESTS

% OF FEED SULPHUR REMOVED

Run No. / Time, Mins.	11	22	23	25	26	27	28-A	28-B	28-C	29	30	32
15	77.3	100	100	86.8	-	-	-	-	-	-	-	-
30	79.3	-	-	62.3	-	75.5	-	-	-	-	-	83.7
35	-	95.0	-	-	-	-	-	-	-	-	-	-
45	-	95.2	-	64.1	-	-	-	-	-	-	-	-
60	-	95.1	-	64.8	-	65.4	-	-	-	-	-	74.4
75	-	-	93.7	61.6	-	-	-	-	-	-	-	-
90	83.2	94.7	92.7	64.5	95.7	-	-	-	-	-	-	-
105	-	-	-	61.5	-	-	-	-	-	-	-	-
120	-	90.4	-	60.9	86.8	-	-	-	-	-	-	-
135	-	-	-	-	-	-	-	-	-	-	-	-
150	82.7	84.7	92.0	-	75	60.2	-	-	-	-	-	-
180	-	86.1	-	-	-	-	-	-	-	-	-	-
210	83.8	-	84.1	-	-	58.4	-	-	-	-	-	-
240	-	-	-	-	-	43.4	-	-	-	-	-	-
270	80.7	-	79.1	-	-	-	-	-	-	-	-	-
300	-	-	76.3	-	-	-	-	-	-	-	-	-
330	-	-	78.3	-	-	-	-	-	-	-	-	-
E10(a) %	82.5	92.5	90.5	61	97.5	62.5	-	-	-	-	-	-
Carbon Rate g/min	-	.15	.69	7.83	2.22	2.84	.82	.89	1.27	.20	.31	6.68

75

(a) E10 = Sulphur removal efficiency at 10% CaO reacted

TABLE C-2

SULPHUR REMOVAL IN FRESH BED BATCH REACTOR TESTS

% FUEL SULPHUR REMOVED

Run No: Time (min)	96	98	99	100	101	102	103	104	105	106	109
10	88.5	-	99.1	99.4	100	100	100	100	100	100	100
20	87.6	72.7	96.8	97.6	84.2	99.2	100	89.4	100	100	-
30	84.5	74.6	91.1	90.4	81.0	99.3	100	87.1	88.3	100	-
40	82.6	74.6	86.2	85.9	79.7	99.5	100	86.6	86.6	100	-
50	82.4	74.3	86.0	83.1	83.2	99.5	100	86.3	86.4	100	84.6
60	82.7	72.7	85.9	83.3	82.6	92.8	100	86.6	-	99.1	-
70	77.8	72.7	85.1	83.2	82.6	92.3	100	86.8	-	98.3	-
80	73.9	74.2	84.5	83.3	81.9	92.1	100	86.4	84.2	97.5	-
90	75.4	73.9	83.6	84.3	81.3	90.5	94.7	86.0	83.8	96.8	80.7
100	76.9	73.5	83.2	-	81.0	90.2	91.0	85.7	87.3	96.8	-
110	78.4	72.7	83.6	-	82.2	89.1	89.1	85.3	85.3	96.7	78.8
120	75.7	71.6	83.6	-	81.1	88.8	88.0	85.0	85.3	96.2	-
130	74.6	72.7	-	-	-	-	86.8	-	88.7	95.8	-
140	72.6	-	-	-	-	-	86.2	-	-	-	-
150	73.4	-	-	-	-	-	84.2	-	-	-	-
160	73.5	-	-	-	-	-	82.7	-	-	-	-
170	69.4	-	-	-	-	-	81.7	-	-	-	-
180	-	-	-	-	-	-	82.2	-	-	-	-
190	76.6	-	-	-	-	-	80.9	-	-	92.9	-
200	69.8	-	-	-	-	-	81.1	-	-	91.9	-
210	78.7	-	-	-	-	-	80.4	-	-	91.3	-
220	76.1	-	-	-	-	-	79.9	-	-	-	-
230	72.6	-	-	-	-	-	79.0	-	-	-	-
240	67.1	-	-	-	-	-	77.8	-	-	-	-
250	70.7	-	-	-	-	-	-	-	-	-	-
260	70.6	-	-	-	-	-	-	-	-	-	-
270	69.8	-	-	-	-	-	-	-	-	-	-
280	69.3	-	-	-	-	-	-	-	-	-	-
290	68.9	-	-	-	-	-	-	-	-	-	-
300	68.7	-	-	-	-	-	-	-	-	-	-
E10[a] %	77.5	73	84	83	81	91	95	86	85	96.5	80.5
Carbon Rate g/min.	-	7.23	7.70	9.76	4.58	-	6.2	3.98	4.69	6.25	-

TABLE C-2

SULPHUR REMOVAL IN FRESH BED BATCH REACTOR TESTS

% FUEL SULPHUR REMOVED

Run. No: Time (min)	110	111	112	113	114	115	118	119	120	121
15	85.6	-	100	100	100	100	84.5	86.4	95.3	100
30	79.7	82.6	88.2	95.5	100	100	83.5	84.7	91.2	100
45	78.6	83.8	85.5	91.5	94.3	100	81.9	84.3	90.7	100
60	75.7	78.8	85.0	91.1	89.4	100	80.0	83.3	90.3	100
75	75.2	78.8	84.7	87.5	86.2	100	82.6	84.4	89.1	100
90	74.5	77.4	85.6	86.1	86.4	99.0	79.0	83.1	88.4	100
105	71.6	75.9	87.8	88.3	85.5	98.4	80.8	82.7	87.0	100
120	-	76.4	84.1	87.9	80.9	94.1	77.6	83.4	86.8	99.8
E10[a] %	73.0	77.0	85.0	87.5	86.2	98.8	79.5	83.5	88.0	100
Carbon Rate g/min.	7.57	2.54	1.11	1.67	-	0.55	6.89	6.61	4.17	0.59

77

(a) E10 = Sulphur removal efficiency at 10% CaO reacted

TABLE C-3

SULPHUR AND METALS PICK UP IN BATCH CYCLIC TESTS
(UK Fuel and Limestone)

Run No.	Cycle	% Fuel Sulphur Removed					Lime Metals Content(1)			Bed Sulphur Content(2) After Regeneration
		15 min	20 min	35 min	40 min	60 min	Sodium ppm	Vanadium ppm	Iron ppm	% by wt.
33	1	-	-	-	-	93.8	160	280	640	1.07
34	2	-	91.0	-	94.7	100	180	500	680	1.42
35	3	-	92.5	-	94.1	93.8	170	660	670	1.75
36	4	-	93.7	-	95.1	91.4	200	840	780	2.21
37	5	-	91.7	-	-	90.2	200	1000	790	2.17
38	6	-	87.8	-	-	83.0	180	1090	910	1.77
39	7	-	-	-	-	-	160	1340	890	2.19
40	8	-	67.1	-	-	70.6	230	1340	890	1.99
41	9	-	-	-	-	-	150	1600	820	1.87
42	10	-	-	-	-	-	230	2000	1000	2.55
43	11	-	-	-	-	-	240	1900	820	2.79
44	12	-	-	-	82.5	73.8	270	2000	890	2.74
45	13	-	-	-	-	81.3	-	-	-	-
46	14	75.7	-	79.3	-	76.7	260	2400	880	2.62
47	15	83.5	-	82.6	-	80.2	260	2400	920	2.28
48	16	73.2	-	74.1	-	70.0	230	2600	1000	2.43
49	17	-	-	74.1	-	76.9	220	2600	1200	2.42
50	18	77.9	-	78.1	-	72.9	340	3200	1300	2.53
51	19	70.8	-	75.6	-	70.9	300	3100	1100	2.52
52	20	69.7	-	73.0	-	72.0	280	3100	1000	2.50
53	21	69.1	-	72.5	-	72.2	270	3100	1100	2.29

78

(1) Measured after each regeneration
(2) All sulphur present as sulphate

TABLE C-3

SULPHUR AND METALS PICK-UP IN BATCH CYCLIC TESTS
(UK Fuel and US Limestone 1691)

Run No.	Cycle	% Fuel Sulphur Removed			Lime Metals Content*			Bed Sulphur Content (% by wt)		
		15 min	35 min	60 min	Sodium ppm	Vanadium ppm	Iron ppm	Total S (60 min)	Total S (A.R.)	Sulphate(A.R.)
54	1	-	98.8	91.4	340	450	4600	3.02	2.01	1.98
55	2	89.3	87.1	89.5	320	630	4700	4.63	2.34	2.24
56	3	81.6	83.3	83.6	300	780	4500	5.44	3.16	2.31
57	4	-	84.7	80.3	180	760	4300	4.10	2.61	2.03
58	5	-	87.5	85.1	250	1050	4800	5.76	2.47	2.39
59	6	78.8	3.7	84.5	260	1130	5000	4.60	2.32	2.30
60	7	87.1	91.1	85.8	260	1380	4900	4.66	2.31	2.29
61	8	-	-	79.4	270	2130	4800	4.00	2.45	2.43
62	9	56.9	74.3	73.9	260	1820	4700	4.47	2.50	2.45
63	10	57.4	73.7	75.1	320	1800	4850	4.62	2.47	2.45
64	11	78.4	73.4	75.6	320	1790	4840	4.50	2.42	2.42
65	12	66.0	68.8	70.3	350	2030	4620	4.73	2.41	2.39
66	13	65.4	74.2	74.4	340	1900	4610	4.65	2.24	2.21
67	14	79.2	79.3	69.2	350	2310	5010	3.68	2.15	2.15
68	15	73.1	71.3	71.5	360	2360	4780	4.32	2.33	2.33
69	16	77.2	73.7	71.3	390	2450	4740	4.47	2.29	2.28
70	17	-	72.3	69.8	370	2030	4850	4.49	2.36	2.14
71	18	73.7	-	73.4	350	2230	4660	4.26	2.20	2.03
72	19	76.9	-	74.2	390	2540	4650	4.16	2.70	2.12

A.R. After Regeneration
* Measured after each regeneration

TABLE C-3

SULPHUR AND METALS PICK-UP IN BATCH CYCLIC TESTS
(UK Fuel and US Limestone 1690)

Run No.	Cycle	% Fuel Sulphur Removed 30 min	45 min	60 min	Lime Metals Content* Sodium ppm	Vanadium ppm	Iron ppm	Bed Sulphur Content (% by wt) Total S (60 min)	Total S (A.R.)	Sulph (A.R.)
78	1	98.8	99.2	93.5	500	210	1450	3.34	1.58	1.58
79	2	92.1	89.3	85.8	460	360	1240	4.11	2.41	2.26
80	3	83.5	83.1	78.7	420	400	2590	4.37	1.81	1.81
81	4	82.9	82.2	79.9	480	430	1430	3.96	1.74	1.71
82	5	90.8	82.7	81.8	310	570	1350	3.83	1.89	1.83
83	6	88.1	86.1	84.8	290	880	5060	3.71	1.93	1.93
84	7	85.9	84.1	80.3	250	760	5050	4.00	1.56	1.56
85	8	87.7	85.7	82.0	290	730	5120	3.72	1.38	1.38
86	9	86.3	82.1	79.1	260	900	5170	3.57	1.43	1.43
87	10	86.0	82.1	77.1	230	1030	5040	-	1.37	1.35
88	11	-	79.2	76.7	260	1280	5100	3.70	1.85	1.84
89	12	78.8	77.7	74.1	230	1390	5070	3.87	2.15	1.97
90	13	77.0	72.8	70.8	260	1340	4780	3.86	1.94	1.84
91	14	68.0	-	65.8	240	1620	4950	3.89	1.95	1.82
92	15	-	-	-	250	1570	4790	3.95	1.81	1.72
93	16	65.6	66.8	64.4	220	2000	4900	4.04	2.29	2.01
94	17	75.9	78.8	73.0	260	1870	4700	4.13	2.29	2.14
95	18	72.7	64.3	64.1	260	2060	4740	4.30	2.13	2.04

A.R. After Regeneration
* Measured after each regeneration

TABLE C-4

CHANGE IN PARTICLE SIZE OF LIME DURING CYCLIC TEST

(UK Fuel and Limestone)

Particle Size Range Microns	% of Bed in Size Range		
	Uncalcined Stone	Cycled Regenerated Lime	
		13 Cycles	20 Cycles
1200-1400	35.6	5.3	3.0
850-1200	57.9	53.3	49.0
600-850	5.8	28.7	32.5
300-600	0.0	10.9	13.8
< 300	0.7	1.8	2.7

TABLE C-5

CHANGE IN PARTICLE SIZE DISTRIBUTION DURING CYCLIC TEST

(US Limestone 1691)

Particle Size Range Microns	% by wt. Bed in Size Range				
			Cycled Regenerated Lime		
	Uncalcined Stone	Calcined Stone	3 Cycles	13 Cycles	19 Cycles
1200-1400	30.5	20.9	30.7	14.4	23.0
850-1200	59.2	57.7	53.2	54.1	50.9
600-850	10.1	17.6	14.9	24.3	23.3
300-600	0	2.3	1.0	5.7	2.5
< 300	0.2	1.4	0.2	1.5	0.3

TABLE C-6

CHANGE IN PARTICLE SIZE DISTRIBUTION DURING CYCLIC TESTS

(US Limestone 1690)

Particle Size Range Microns	% by wt. Bed in Size Range				
		Cycled Regenerated Lime			
	Uncalcined Stone	1 Cycle	5 Cycles	10 Cycles	18 Cycles
1200-1400	26.5	29.0	13.8	14.1	21.7
850-1200	64.1	55.4	49.8	49.9	48.2
600-850	8.9	13.8	24.3	24.3	20.4
300-600	0.1	1.2	7.0	8.3	5.9
< 300	0.4	0.6	5.1	3.4	3.8

TABLE C-7

COMPOSITION OF GASIFIER PRODUCT

DRY GAS BASIS

Component	Run No:	Composition of Dry Gas, % by Vol. 53	65	86
Oxygen		0	0	0
Nitrogen		64.0	57.0	62.0
Carbon Monoxide		10.4	10.3	8.3
Carbon Dioxide		10.1	9.7	10.9
Hydrogen		4.2	10.0	7.4
Methane		4.4	6.5	5.1
C_2		5.4	5.8	5.4
C_3		0.3	0.5	0.8
C_4		0.2	0.2	0.1

APPENDIX D

COLD GASIFIER MODEL SOLIDS TRANSFER AND ATTRITION RESULTS

TABLE D-1

RESULTS OF SOLIDS TRANSFER TESTS
BRICK DUST, GASIFIER TO REGENERATOR

Pulse Length sec.	On Time % of Total	Solids Rate lb/Hr.	Solids/Air Ratio lb/ft3	Fines Recovery lb/Hr.
1	6.7	76.5	0.57	2.6
1	10	160.2	1.32	5.4
1	17	2.15	1.5	3.0
1	20	292	1.97	5.8
1	25	324	2.15	2.9
1	33	579	2.14	1.8
1	50	759	2.53	2.6
2	10	75	0.43	0.5
2	20	183	1.23	1.5
2	33	201	1.25	0.6
2	40	302	2.03	1.9
2	50	410	1.85	2.5
2	67	492	1.88	1.3
4	17	69	.53	0.8
4	33	128	.99	1.6
4	50	289	1.88	2.3
4	57	356	2.2	1.9
5	33	213	1.05	1.6
5	42	240	1.81	2.5
5	63	453	2.04	5.1

TABLE D-2

CHANGE IN PARTICLE SIZE OF COLD UNIT BRICK DUST

Particle Size Range Microns	Size Distribution wt % in Size Range			
	Fresh Brick Dust	Aged Brick Dust		
		5 hr	10 hr	130 hr
850 - 1200	92.8	81.3	80.8	25.1
600 - 850	6.9	16.1	15.9	54.3
300 - 600	0.1	1.5	1.4	18.2
<300	0.2	1.1	2.0	2.4